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<p>(21) International Application Number: PCT/US98/11019</p> <p>(22) International Filing Date: 29 May 1998 (29.05.98)</p> <p>(30) Priority Data:</p> <table> <tr> <td>97/06917</td> <td>30 May 1997 (30.05.97)</td> <td>FR</td> </tr> <tr> <td>60/082,974</td> <td>24 April 1998 (24.04.98)</td> <td>US</td> </tr> <tr> <td>60/083,005</td> <td>24 April 1998 (24.04.98)</td> <td>US</td> </tr> </table> <p>(71) Applicant: MONSANTO COMPANY [US/US]; 800 N. Lindbergh Boulevard, St. Louis, MO 63167 (US).</p> <p>(72) Inventors: SOULA, Gérard, G.; 33, rue de Nungesser, F-69330 Meyzieux (FR). MEYRUEIX, Rémi; 42, rue H. Berlizoz, Le Bois Saint Rambert, F-69009 Lyon (FR). LEMERCIER, Alain, J., L.; 3, rue Hector Berlizoz, F-69720 Saint Bonnet de Mure (FR). CAISSE, Philippe, G.; 41, rue de la Batterie, F-69500 Bron (FR). WARD, Anthony, J., I.; 821 Westwood Drive, Clayton, MO 63105 (US). GILLESPIE, Jane, L.; 7229 Cornell, St. Louis, MO 63130 (US). BRINKER, Ronald, J.; 925 Oakgrove Park Court, Ellisville, MO 63021 (US).</p> <p>(74) Agent: GOODMAN, Kenneth, D.; Arnold, White &amp; Durkee, P.O. Box 4433, Houston, TX 77210 (US).</p>		97/06917	30 May 1997 (30.05.97)	FR	60/082,974	24 April 1998 (24.04.98)	US	60/083,005	24 April 1998 (24.04.98)	US	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b>  <i>With international search report.  Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
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<p>(54) Title: PROCESS AND COMPOSITIONS PROMOTING BIOLOGICAL EFFECTIVENESS OF EXOGENOUS CHEMICAL SUBSTANCES IN PLANTS</p> <p style="text-align: center;"> <span style="margin-left: 20px;">(I)</span> </p> <p>(57) Abstract</p> <p>A plant treatment composition for application of an anionic exogenous chemical substance such as glyphosate herbicide to foliage of a plant is provided. The composition is a colloidal suspension having supramolecular aggregates dispersed in an aqueous application medium. The supramolecular aggregates comprise one or more amphiphilic salt(s) having anions of the exogenous chemical substance and cations derived by protonation of one or more amine compound(s) each having formula (I), wherein R<sup>1</sup> and R<sup>2</sup> are independently linear hydrocarbyl chains each having 6 to about 22 carbon atoms, and R<sup>3</sup> is hydrogen, a C<sub>1-5</sub> hydrocarbyl group or a linear hydrocarbyl chain no longer than R<sup>1</sup> and no longer than R<sup>2</sup>. The exogenous chemical substance is present in the composition in a first molar amount X<sup>1</sup> in the form of said amphiphilic salt(s) and in a zero or second molar amount X<sup>2</sup> in the form of one or more salt(s) having anions of the exogenous chemical substance and cations derived from one or more base(s) other than an amine compound of formula (I). X<sup>1</sup> as a fraction of (X<sup>1</sup> + X<sup>2</sup>) is about 0.01 to 1. Also provided are a liquid concentrate composition which, upon dilution with water, forms a plant treatment composition, and a process for making such a liquid concentrate composition. Plant treatment compositions of the invention are useful for eliciting a desired biological activity, for example herbicidal activity, in a plant.</p>												

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PROCESS AND COMPOSITIONS PROMOTING BIOLOGICAL EFFECTIVENESS  
OF EXOGENOUS CHEMICAL SUBSTANCES IN PLANTS

FIELD OF THE INVENTION

The field of the present invention is that of exogenous chemical substances applied  
5 to foliage of plants, and relates particularly to a process and to compositions applied by  
that process for promoting biological effectiveness of such exogenous chemical  
substances.

The term "exogenous chemical substance" as used herein means a chemical  
substance, whether naturally or synthetically obtained, which is applied to a plant to result  
10 in expressing a desired biological activity. The term "biological activity" as used herein  
means elicitation of a stimulatory, inhibitory, regulatory, therapeutic, toxic or lethal  
response in the plant or in a pathogen, parasite or feeding organism present in or on the  
plant. Examples of exogenous chemical substances include, but are not limited to,  
chemical pesticides (such as herbicides, algicides, fungicides, bactericides, viricides,  
15 insecticides, miticides, nematicides and molluscicides), plant growth regulators, fertilizers  
and nutrients, gametocides, defoliants, desiccants, mixtures thereof and the like.

The term "biological effectiveness" is used herein to denote the degree to which a  
desired biological activity is expressed upon application of an exogenous chemical  
substance to foliage of a plant, or alternatively to denote the dosage or rate of application  
20 of the exogenous chemical substance that results in the desired biological activity being  
expressed to a given degree. For example, where the exogenous chemical substance is a  
herbicide, biological effectiveness can be measured by the degree of inhibition of plant  
growth resulting from application of a particular rate of the herbicide, or by the application  
rate of the herbicide required to cause a particular degree of inhibition, e.g., 50% or 85%  
25 inhibition. Thus increased or enhanced biological effectiveness of a herbicide can be  
exhibited for example as an increased level of plant growth inhibition at a given rate of the  
herbicide, or as a reduction in the minimum rate of the herbicide giving a certain threshold  
level of plant growth inhibition.

BACKGROUND OF THE INVENTION

30 For many purposes in agriculture and related endeavors it is desired to treat plants  
with exogenous chemical substances of various kinds. Many exogenous chemical

substances are applied to foliage (*i.e.*, leaves and other non-woody above-ground parts) of a plant, and have a site of action in the plant either close to or remote from the locus of application. Such substances are referred to herein as foliar-applied exogenous chemical substances.

5       Typically, when an exogenous chemical substance is applied to foliage by plant treatment processes known in the art, only a small portion of the amount applied reaches sites of action in the plant where a desired biological activity of the exogenous chemical substance can be usefully expressed. It is therefore a major desideratum in agriculture and related endeavors to enhance the efficiency of delivery of foliar-applied exogenous  
10      chemical substances to their sites of action in plants, and thereby to enhance the biological effectiveness of the exogenous chemical substance for the purpose for which the exogenous chemical substance is used.

Application to foliage of an exogenous chemical substance by processes known in the art does not universally result in inefficient delivery to sites of action. In some  
15      situations such processes provide excellent biological effectiveness, even at a low use rate of the exogenous chemical substance. In other situations the same processes, using the same rate of the exogenous chemical substance, provide inadequate biological effectiveness. Thus, these processes are inconsistent in the result they provide, or they cannot be relied upon to provide the desired result.

20      A problem is that it is seldom possible to identify in advance those situations where good biological effectiveness will be obtained, partly because so many factors influence efficiency of delivery. These factors include weather (temperature, relative humidity, daylength, cloudiness, precipitation, wind, *etc.*) preceding, during and following application, soil conditions (fertility, aeration, *etc.*), plant growth stage, health and  
25      physiological status, equipment-related inaccuracies in application, and other factors. Therefore, to help ensure reliable or consistent biological effectiveness of a foliar-applied exogenous chemical substance, the user typically applies the substance at a higher rate than truly necessary in the majority of situations.

30      Variability in biological effectiveness in field conditions is an especially troublesome problem in the case of exogenous chemical substances that are acids, and are typically formulated as water-soluble salts in which the exogenous chemical substance is present in an anionic form. Sometimes by converting such acid substances to esters, this

variability can be moderated; however, in many cases esters show reduced biological effectiveness, for example due to inadequate conversion back to the parent acid once inside the treated plant. There remains a strong need for enhanced biological effectiveness, and enhanced reliability of biological effectiveness, of foliar-applied exogenous chemical substances, particularly anionic exogenous chemical substances.

The term "anionic exogenous chemical substance" as used herein means an exogenous chemical substance whose molecular structure includes one or more acid, or proton-donating, sites, and is therefore capable of forming an anion in the presence of a proton acceptor. The term therefore embraces substances that are zwitterionic. In describing an exogenous chemical substance as "anionic" herein, it is not implied that the exogenous chemical substance is necessarily in anionic form or that it is dissociated.

Benefits of a process providing greater reliability of biological effectiveness include an ability to reduce rates of application of exogenous chemical substances without sacrificing consistency of biological effectiveness. Pressures felt by the agricultural industry to reduce pesticide, particularly herbicide, usage are well evidenced by symposia on the subject, such as that held in 1993 by the Weed Science Society of America and documented in *Weed Technology* 8, 331-386 (1994). Reduced use rates bring rewards not only environmentally but also economically, as the cost per unit area treated decreases.

Foliar-applied exogenous chemical substances have frequently been applied together with amphiphilic materials, particularly amphiphilic surface-active agents, otherwise known as surfactants. Surfactants can influence biological effectiveness of a foliar-applied exogenous chemical substance in numerous ways.

When a dilute aqueous composition of an exogenous chemical substance is applied to foliage by conventional hydraulic spraying, the presence of surfactant in the dilute aqueous composition can alter the size distribution of the spray droplets, typically increasing the percentage of spray volume in the form of small droplets and reducing the percentage of spray volume in the form of large droplets. As smaller droplets have lower momentum than larger droplets, these smaller droplets are less likely to rebound from a foliar surface and consequently are more likely to be retained on that surface. Spray retention can also be facilitated by adhesion between surfactant molecules in a spray droplet and the foliar surface, which in most plants is waxy and hydrophobic. This adhesion reduces not only rebound but also run-off of spray droplets from the foliar

surface. Surfactants also tend to increase the area of contact between a spray droplet and a foliar surface, and in many cases enhance penetration of an exogenous chemical substance from the droplet into and through cuticles of leaves to reach internal leaf tissues.

Through these and perhaps other effects, amphiphilic materials including surfactants have long been known to increase the biological effectiveness of exogenous chemical substances. It is therefore commonplace for one or more surfactants to be included in commercial formulations of foliar-applied exogenous chemical substances, even in formulations that do not require the presence of surfactants for acceptable physical stability or handling properties, for example as emulsifying or suspending agents or dispersants.

One of the most extensively studied of foliar-applied anionic exogenous chemical substances, from the point of view of the role of surfactants in enhancing biological effectiveness, is the herbicide glyphosate. As well as being a phytotoxic agent, glyphosate has been used as a plant growth regulator.

Glyphosate in its strict sense is an acid compound, N-phosphonomethylglycine, but the word "glyphosate" is herein used in a less restrictive sense, except where the context dictates otherwise, to encompass not only glyphosate acid but also salts, adducts and esters thereof, and compounds which are converted to glyphosate in plant tissues or which otherwise provide glyphosate ions. In most commercial formulations of glyphosate, the glyphosate is present as a water-soluble salt. In this respect, glyphosate is typical of most exogenous chemical substances that are acids or that form anions.

Herbicidal salts of glyphosate are disclosed, for example, in U.S. Patent No. 3,799,758 to Franz, U.S. Patent No. 3,853,530 to Franz, U.S. Patent No. 4,140,513 to Prill, U.S. Patent No. 4,315,765 to Large, U.S. Patent No. 4,405,531 to Franz, U.S. Patent No. 4,481,026 to Prisbylla and U.S. Patent No. 4,507,250 to Bakel. In most of the salts disclosed, the counterion to glyphosate anion is a relatively low molecular weight, non-amphiphilic cation. Typical of such salts are alkali metal, for example sodium and potassium, salts; ammonium salt; C<sub>1-6</sub> alkylammonium, for example dimethylammonium and isopropylammonium, salts; C<sub>1-6</sub> alkanolammonium, for example ethanolammonium, salts, C<sub>1-6</sub> alkylsulfonium, for example trimethylsulfonium, salts; and sulfoxonium salts.

Commercial formulations of glyphosate salts include, for example, Roundup® brand, Accord® brand and Roundup® Ultra brand herbicides of Monsanto Company,

which contain the isopropylammonium salt, Roundup® Dry brand and Rodeo® brand herbicides of Monsanto Company, which contain the ammonium salt, Roundup® Geoforce brand herbicide of Monsanto Company, which contains the sodium salt, and Touchdown® brand herbicide of Zeneca, which contains the trimethylsulfonium salt.

5        Salts of glyphosate with higher molecular weight, amphiphilic cations have also been disclosed. Such amphiphilic cations include those having a hydrophilic moiety such as an ammonium, ethanolammonium, polyoxyethylene ammonium, or sulfonium group, and a hydrophobic moiety comprising 1 to 4 hydrocarbyl groups having in total more than 10 6 carbon atoms. For example, above-cited U.S. Patent No. 4,405,531, the disclosure of which is incorporated herein by reference, discloses a wide range of primary, secondary and tertiary ammonium salts of glyphosate wherein the cation is amphiphilic as defined immediately above but has a molecular weight of less than about 300. International Publication No. WO 83/03608, European Patent Application No. 0 124 351 and U.S. Patent No. 4,431,594 disclose various quaternary ammonium salts of glyphosate wherein 15 the cation is amphiphilic. U.S. Patent No. 5,668,085 discloses salts of glyphosate with amphiphilic cations derived from polyoxyethylene C<sub>8-22</sub> tertiary alkylamine surfactants, a specifically disclosed example being the N-cocoalkyl-N,N-diethanolammonium salt of glyphosate where "cocoalkyl" refers to a mixture of predominantly C<sub>12</sub> and C<sub>14</sub> alkyl chains, derived from coconut oil.

20        Glyphosate as a herbicide has many advantages, particularly environmental advantages including biodegradability and low ecotoxicity. However, studies have shown that even the most biologically effective formulations of glyphosate presently in use do not deliver glyphosate efficiently to sites in the plant where the glyphosate exerts its phytotoxic effect. Typically, only a small fraction of the applied herbicide arrives at such 25 sites. The term "biodisponibilité" (approximately equivalent in meaning to the English word "bioavailability") is used in French patent application no. 97-06917 from which the present application claims priority, to refer to this fraction.

30        The small fraction of applied glyphosate which reaches sites of phytotoxic action is related to the fact that the glyphosate must go through several barriers. Among these, one of the most important is believed to be the lipophilic cuticle on the foliar surface to which the glyphosate is applied. It has therefore been theorized that it would be desirable to place the glyphosate into an amphiphilic medium which would provide greater

compatibility between the lipophilic cuticle and the hydrophilic glyphosate, and thereby facilitate penetration of glyphosate into and through the cuticle. Similar thinking has been applied to other exogenous chemical substances, particularly those typically formulated as water-soluble salts.

5 That the concept of an amphiphilic medium as an aid to cuticular penetration and thereby enhanced biological effectiveness, for example of glyphosate, has validity is demonstrated by many studies in which foliar uptake or effectiveness has been enhanced by surfactants. An extensive study by Wyrill & Burnside, *Weed Science* 25, 275-287, 1977 led to a conclusion that "an effective surfactant is a critical component of any  
10 glyphosate spray mixture", but noted great variation among surfactant types in the degree of enhancement of herbicidal effectiveness afforded. In general, cationic surfactants gave greater enhancement than nonionic surfactants. Data are reported in International Publication No. WO 98/06259 for a wide range of cationic, nonionic, anionic and amphoteric surfactants applied either in mixture with, or in sequence following, a  
15 glyphosate composition.

Another approach to providing an amphiphilic medium has been to apply glyphosate together with a lipophilic agent, such as an oil, in the form of a water-in-oil emulsion or microemulsion. Such emulsions or microemulsions are disclosed in European Patent Application No. 0 379 852, U.S. Patent No. 4,853,026 and U.S. Patent No.  
20 5,248,086. A disadvantage of such microemulsions is that, when provided as concentrate compositions, they are subject to the phenomenon of breaking of the emulsion upon dilution with water to concentrations suitable for application, for example, 5 grams of glyphosate, expressed as acid equivalent, per liter (g a.e./l). In other words, water-in-oil microemulsions tend not to withstand dilution in water. The failure of such  
25 microemulsions to provide improved cuticular penetration is perhaps related to this inability to withstand dilution.

Oil-in-water macroemulsion formulations of glyphosate have also been investigated. In these macroemulsions, the majority of the glyphosate is present in the continuous aqueous phase, as shown, for example, in European Patent Application No.  
30 0 485 207. Such macroemulsions, in which the glyphosate and the lipophilic component are segregated, do not therefore provide glyphosate in an amphiphilic form, and have generally not enhanced delivery of glyphosate to its sites of phytotoxic action in the plant.

A different approach, illustrated in European Patent Specification No. 0 148 169, is to encapsulate a water-soluble herbicide such as glyphosate in a polymeric shell by interfacial polycondensation. In this technique, a water-in-oil emulsion having a lipophilic emulsifier based on alkylated polyvinylpyrrolidone is used. Polymerization to form the shell, by reaction of comonomers, occurs at the oil-water interface of the emulsion containing the herbicide, resulting in formation of a shell that encapsulates the herbicide.

All of the approaches summarized above, including formulating an anionic exogenous chemical substance as an amphiphilic salt, have met with limited success in overcoming the barriers to delivery of the exogenous chemical substance to its sites of biological action in the plant. It is an objective, therefore, of the present invention to provide a new composition or formulation of an exogenous chemical substance, in particular an anionic exogenous chemical substance, that can provide superior biological effectiveness when applied to foliage of a plant.

Another objective of the invention is to provide a composition or formulation of an exogenous chemical substance, in particular an anionic exogenous chemical substance, that is economical and simple to make.

Another objective of the invention, particularly as it applies to the herbicide glyphosate, is to provide a composition or formulation that meets the previously stated objectives while permitting maintenance of the non-ecotoxic and biodegradable character of glyphosate.

Another objective of the invention is to provide a composition or formulation of an exogenous chemical substance, particularly an anionic exogenous chemical substance, that can be applied in a dilute aqueous medium and does not lose its beneficial properties at high rates of dilution.

Another objective of the invention is to provide a convenient and economical method for the preparation of a composition or formulation that meets the objectives stated above.

These and other objectives have been satisfied through design of a new approach for promoting transport of an anionic exogenous chemical substance into plants via foliage, and thereby promoting biological effectiveness of the exogenous chemical substance. This approach, as set out more fully below, involves the production of a

colloidal dispersion of supramolecular aggregates, or nanoparticles, containing the exogenous chemical substance wholly or partly in the form of an amphiphilic salt thereof.

#### DESCRIPTION OF THE FIGURE

Figure 1 is a transmission electron micrograph (magnification 28,000 $\times$ ) of a colloidal suspension of supramolecular aggregates containing an amphiphilic salt of glyphosate prepared according to Example 1 hereof. The supramolecular aggregates appear as approximately spherical beads, most easily visible in the darker areas of the micrograph. They range widely in diameter, with most falling in a range from about 50 to about 500 nm.

#### 10 SUMMARY OF THE INVENTION

A plant treatment composition for application to foliage of a plant to elicit a desired biological response is now provided, comprising an aqueous application medium, in which supramolecular aggregates are colloidally dispersed. The supramolecular aggregates comprise one or more amphiphilic salt(s) of an exogenous chemical substance having anions of an anionic exogenous chemical substance and cations derived by protonation of one or more amine compound(s) each having the formula (I)



wherein R<sup>1</sup> and R<sup>2</sup> are independently linear hydrocarbyl chains each having 6 to about 22 carbon atoms, and R<sup>3</sup> is hydrogen, a C<sub>1-5</sub> hydrocarbyl group or a linear hydrocarbyl chain no longer than R<sup>1</sup> and no longer than R<sup>2</sup>. The exogenous chemical substance is present in the composition in a first molar amount X<sup>1</sup> in the form of said amphiphilic salt(s) and in a zero or second molar amount X<sup>2</sup> in the form of one or more salt(s) having anions of the exogenous chemical substance and cations derived from one or more base(s) other than an amine compound of formula (I). The total molar amount (X<sup>1</sup> + X<sup>2</sup>) of the exogenous chemical substance in salt form is sufficient to elicit the desired biological response when the composition is applied to the foliage of the plant at a rate from about 10 to about 1000 liters per hectare (l/ha). X<sup>1</sup> as a fraction of (X<sup>1</sup> + X<sup>2</sup>) is about 0.01 to 1.

In one illustrative embodiment, the anionic exogenous chemical substance is N-phosphonomethylglycine.

In one embodiment of the invention, the amine compound of formula (I) has a molecular weight of about 240 to about 700. In another embodiment of the invention the 5 amine compound of formula (I) has a molecular weight greater than about 300 and not greater than about 560.

The second molar amount, if present, is preferably present in the form of one or more salt(s) having monovalent cations selected from alkali metal, ammonium, C<sub>1-5</sub> alkylammonium, C<sub>1-5</sub> alkanolammonium, C<sub>1-5</sub> alkanolalkylammonium and C<sub>1-5</sub> 10 alkylsulfonium cations, and cations derived from an amine compound of formula (II):



wherein R<sup>4</sup> and R<sup>5</sup> are independently hydrogen, methyl groups or hydrocarbyl chains each having 2 to 5 carbon atoms, and R<sup>6</sup> is a linear hydrocarbyl chain having 6 to about 22 carbon atoms.

15 In one embodiment of the invention, X<sup>1</sup> as a fraction of (X<sup>1</sup> + X<sup>2</sup>) is about 0.01 to about 0.2. In another embodiment, X<sup>1</sup> as a fraction of (X<sup>1</sup> + X<sup>2</sup>) is about 0.3 to 1.

A liquid, preferably aqueous, concentrate composition is also provided, which when diluted with a suitable amount of water forms a plant treatment composition as described above. A contemplated liquid concentrate composition contains in total at least 20 about 5% by weight and up to about 40% or more by weight of the exogenous chemical substance expressed as acid equivalent (a.e.).

Also provided is a process for making liquid concentrate compositions of the invention, comprising a neutralizing step and a conditioning step.

The neutralizing step comprises neutralization of a first molar amount X<sup>1</sup> of an 25 anionic exogenous chemical substance with one or more amine compound(s) of formula (I) in a liquid, preferably aqueous, medium with agitation to make a liquid composition containing one or more amphiphilic salt(s) of the exogenous chemical substance. Optionally the neutralizing step further comprises introducing to the liquid composition, with agitation, a second molar amount X<sup>2</sup> of the exogenous chemical substance in the form

of one or more salt(s) other than an amphiphilic salt formed by neutralizing the exogenous chemical substance with an amine compound of formula (I).  $X^1$  as a fraction of  $(X^1 + X^2)$  is about 0.01 to 1. The salt(s) of the second molar amount of the exogenous chemical substance can be made *in situ* by neutralizing, in the liquid medium with agitation, this 5 second molar amount with one or more base(s) other than an amine compound of formula (I), before, during or after neutralization of the first molar amount; alternatively such salt(s) can be prepared separately by processes known in the art and added to the liquid medium before, during or after neutralization of the first molar amount.

The conditioning step comprises continuing the agitation of the liquid composition 10 until supramolecular aggregates comprising amphiphilic salt(s) of the exogenous chemical substance formed by neutralizing the exogenous chemical substance with an amine compound of formula (I) are colloidally dispersed in the liquid medium.

Where an anionic exogenous chemical substance has a molecular structure with only one acid site, the term "neutralizing" is to be understood to mean reacting 15 substantially equimolar amounts of acid and base. Where an anionic exogenous chemical substance has a molecular structure with two or more acid sites, as is the case for example with N-phosphonomethylglycine, the term "neutralizing" is to be understood to mean reacting each mole of acid with about 1 to about 2 moles of base to form a monobasic salt, a dibasic salt, or a mixture thereof.

20 Also provided is a process for eliciting a desired biological activity in a plant or in a pathogen, parasite or feeding organism present in or on the plant, comprising a step of applying to foliage of the plant a biologically effective amount of a plant treatment composition as provided herein.

Contemplated compositions have numerous benefits and advantages.  
25 When applied to foliage of plants according to the process of the invention, a contemplated composition provides enhanced biological effectiveness by comparison with commercial standard formulations of the same exogenous chemical substance. At equal application rates of the exogenous chemical substance, a contemplated composition elicits a greater biological response than a commercial standard formulation. To obtain a given 30 level of biological response, a lower application rate is required of the exogenous chemical substance when applied in the form of a contemplated composition than in the form of a commercial standard formulation.

A contemplated composition is biologically effective at a given application rate on a broader spectrum of target species than commercial standard formulations.

A contemplated composition provides greater reliability or consistency of biological effectiveness in a range of environmental conditions than commercial standard formulations.

A contemplated composition is more rainfast, *i.e.*, its biological effectiveness is less likely to be reduced by incidence of rain or overhead irrigation occurring within a short period, for example up to about 6 hours, after application, than commercial standard formulations.

10 A contemplated composition provides an observable biological response in a shorter period after application than commercial standard formulations.

#### DETAILED DESCRIPTION OF THE INVENTION

##### Exogenous chemical substances

Examples of anionic exogenous chemical substances that can be used in compositions of the present invention include, but are not limited to, chemical pesticides (such as herbicides, algicides, fungicides, bactericides, viricides, insecticides, aphicides, miticides, nematicides and molluscicides), plant growth regulators, fertilizers and nutrients, gametocides, defoliants, desiccants, mixtures thereof and the like. Although the disclosure herein relates to "an exogenous chemical substance", it is to be understood that more than one exogenous chemical substance can be included if desired in a composition of the invention.

A preferred group of anionic exogenous chemical substances consists of those that are normally applied post-emergence to foliage of plants, *i.e.*, foliar-applied anionic exogenous chemical substances. An especially preferred group of foliar-applied anionic exogenous chemical substances consists of those that are systemic in plants, that is, translocated to some extent from their point of entry in the foliage to other parts of the plant where they can usefully exert their desired biological effect.

Especially preferred among these are herbicides, plant growth regulators and nematicides, particularly those that have a molecular weight, excluding counterions, of less than about 300.

Among such compounds, an even more preferred category consists of nematicides such as those disclosed in U.S. Patent No. 5,389,680, the disclosure of which is incorporated herein by reference. Preferred nematicides of this group are 3,4,4-trifluoro-3-butenoic acid or N-(3,4,4-trifluoro-1-oxo-3-butenyl)glycine.

5 In one embodiment, the exogenous chemical substance is a herbicide. Suitable herbicides include, without restriction, acifluorfen, asulam, benazolin, bentazon, bilanafos, bromacil, bromoxynil, chloramben, clopyralid, 2,4-D, 2,4-DB, dalapon, dicamba, dichlorprop, diclofop, endothall, fenac, fenoxaprop, flamprop, fluazifop, flumiclorac, fluoroglycofen, fomesafen, fosamine, glufosinate, glyphosate, haloxyfop, imazameth,  
10 imazamethabenz, imazapyr, imazaquin, imazethapyr, ioxynil, MCPA, MCPB, mecoprop, methylarsonic acid, naptalam, nonanoic acid, picloram, quinclorac, quizalofop, sulfamic acid, 2,3,6-TBA, TCA and triclopyr. Especially preferred herbicides are those whose molecular structure comprises at least one of each of amine, carboxylate, and either phosphonate or phosphinate functional groups. This category includes the herbicides  
15 N-phosphonomethylglycine (glyphosate) and DL-homoalanin-4-yl(methyl) phosphinate (glufosinate). Another preferred group of herbicides are those of the imidazolinone class, including imazameth, imazamethabenz, imazapyr, imazaquin and imazethapyr.

The invention is illustrated herein by particular reference to glyphosate. Although glyphosate has three acid sites, and can therefore form tribasic salts, preferred aqueous compositions have a pH value not greater than about 8, at which pH value the fraction of glyphosate existing as a tribasic salt is negligibly small. Only the two acid sites that are significantly deprotonated at pH 8 are therefore considered herein. One of these is on the phosphonate moiety, and the other is on the carboxylate moiety, of the glyphosate molecule.  
20

25 For convenience and brevity herein, glyphosate acid is sometimes referred to as GH<sub>2</sub>. Monovalent glyphosate anions, such as predominate for example at around pH 4, are referred to as GH<sup>-</sup>. Divalent glyphosate anions, such as predominate for example at pH 7-8, are referred to as G<sup>2-</sup>.

In plant treatment compositions of the invention, the amount of exogenous chemical substance present, in all forms thereof, is sufficient when applied to foliage of a plant to elicit the desired biological activity. Such compositions are sometimes referred to as "spray compositions", "sprayable compositions" or "ready-to-use compositions" and  
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typically contain about 0.02% by weight to about 2% by weight of the exogenous chemical substance, expressed as acid equivalent (a.e.). For some purposes such compositions can contain up to about 5% a.e. by weight or even 10% a.e. by weight.

In liquid concentrate compositions of the invention, the amount of exogenous chemical substance present, in all forms thereof, provides, upon dilution in a suitable volume of water and application of the diluted composition to foliage of a plant, a sufficient amount to elicit the desired biological activity. Liquid concentrate compositions contain about 10% a.e. by weight to about 40% a.e. by weight or more of the exogenous chemical substance, in all forms thereof present.

As a significant portion of the cost of a packaged liquid concentrate composition is the volume-related cost of packaging, transport and storage, it is desirable to increase to the maximum practicable extent the concentration, or "loading", of exogenous chemical substance in the composition. Generally the factor that limits loading is physical stability of the composition under a range of storage conditions. The upper limit of loading depends on the nature and concentration of other ingredients in the composition and can be readily determined by routine experimentation using procedures known in the art.

Amphiphilic salt(s) of the first molar amount of the exogenous chemical substance

Compositions of the invention contain supramolecular aggregates comprising amphiphilic salt(s) formed by neutralization of a first molar amount  $X^1$  of the anionic exogenous chemical compound by one or more amine compound(s) each having the formula (I)



wherein  $R^1$  and  $R^2$  are independently linear hydrocarbyl chains each having 6 to about 22 carbon atoms, and  $R^3$  is hydrogen, a  $C_{1-5}$  hydrocarbyl group or a linear hydrocarbyl chain no longer than  $R^1$  and no longer than  $R^2$ . In the formula for the amine compound,  $R^1$  and  $R^2$  preferably each have at least 8, more preferably at least 10, carbon atoms.  $R^3$  is preferably hydrogen or a  $C_{2-5}$  hydrocarbyl group, more preferably hydrogen or a  $C_{1-3}$  alkyl group. Even more preferably,  $R^1$  and  $R^2$  are saturated or unsaturated chains each having

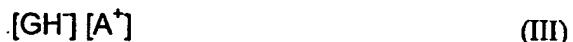
independently 12, 14, 16 or 18 carbon atoms and R<sup>3</sup> is hydrogen or a methyl group. Typically R<sup>1</sup> and R<sup>2</sup> chains are alike, and are derived from lauric, myristic, palmitic, stearic, oleic, linolenic, linoleic or other natural fatty acids, with saturated chains such as lauryl, myristyl, palmityl or stearyl groups being preferred.

5 In one embodiment of the invention, the molecular weight of the amine compound of formula (I) is about 240 to about 700. In a particular embodiment of the invention which has been found to provide especially pronounced enhancement of biological effectiveness, the molecular weight of the amine compound of formula (I) is greater than about 300, for example greater than about 330, and not greater than about 560.

10 Particularly preferred examples of amine compounds of formula (I) include dilaurylamine (molecular weight 353), available as Noram<sup>TM</sup> 2C, N,N-dilauryl-N-methylamine (molecular weight 367), available as Noram<sup>TM</sup> M2C, and N,N-distearyl-N-methylamine (molecular weight 535), available as Noram<sup>TM</sup> M2SH, all from CECA S.A. of Paris, France.

15 Normally, by design, only one amine compound of formula (I) is used to prepare an amphiphilic salt of the exogenous chemical substance. However, as at least the R<sup>1</sup> and R<sup>2</sup> groups of the amine compound are often derived from natural sources such as coconut oil, palm oil, beef tallow, etc., commercial preparations of such amine compounds can contain a range of hydrocarbyl chain lengths, sometimes with varying degrees of  
20 unsaturation. Thus when amounts of an amine compound of formula (I) are specified herein, it is to be understood that such amounts are inclusive of other amine compounds of formula (I) present in the amine compound preparation used.

An amine compound of formula (I) is sometimes represented in its protonated (cationic) form herein as A<sup>+</sup>. An amphiphilic monobasic salt of glyphosate with cations  
25 derived from an amine compound of formula (I) can therefore be represented by formula (III):



and a dibasic salt by formula (IV):



30 In some embodiments of the invention, the amphiphilic salt(s) of the exogenous chemical substance and one or more amine compound(s) of formula (I) are the only salts of the exogenous chemical substance present in the composition. In such embodiments the

first molar amount  $X^1$  of the exogenous chemical substance represents all of the exogenous chemical substance present in salt form, *i.e.*,  $X^2 = 0$ . The amount of  $A^+$  present in such embodiments is about 1 mole per mole of exogenous chemical substance in the case of a monobasic salt, and about 2 moles per mole of exogenous chemical substance in the case of a dibasic salt. A mixture of monobasic and dibasic salts can be present, and in such a case the amount of  $A^+$  present can range from about 1 to about 2 moles per mole of exogenous chemical substance. Where the exogenous chemical substance is glyphosate, a mixture of amphiphilic salts of formulas (III) and (IV) can be present.

For most purposes, even where the exogenous chemical substance is glyphosate, it is preferred that the monobasic salt predominate in the composition; in other words, that the amount of  $A^+$  present be not substantially greater than 1 mole per mole of exogenous chemical substance. At higher mole ratios of  $A^+$  to exogenous chemical substance, it becomes more difficult to obtain the desired high loading of exogenous chemical substance in a concentrate composition. Thus in a glyphosate composition of the invention where  $X^2 = 0$ , it is preferred that the amphiphilic salt of formula (III) predominate. For example, it is preferred that the mole ratio of (III) to (IV) be about 80:20 to 100:0. This corresponds to a mole ratio of  $A^+$  to exogenous chemical substance of about 1:1 to about 1.2:1.

Where one or more salt(s) of a second molar amount of the exogenous chemical substance are present in a composition of the invention, *i.e.*,  $X^2 > 0$ , the amount of amphiphilic salt(s) comprising  $A^+$  cations is correspondingly reduced as a fraction of all salts of the exogenous chemical substance present. In general, to provide the benefits of the present invention, the amount of  $A^+$  present, on a molar basis, should be not less than about 1% of all cations forming salts with the exogenous chemical substance, *i.e.*,  $X^1$  as a fraction of  $(X^1 + X^2)$  is about 0.01 to 1.

In one embodiment of the invention,  $X^1$  represents a relatively small fraction of  $(X^1 + X^2)$ , for example about 0.01 to about 0.2. In this embodiment, it is a primary objective to prepare a stable concentrate composition with a high loading of the exogenous chemical substance on an acid equivalent basis. As the amine compound(s) from which the  $A^+$  cations are derived have relatively high molecular weight, it is difficult to achieve the desired high loading except where relatively low molecular weight  $B^+$  cations, for example sodium, ammonium or isopropylammonium cations, predominate.

In another embodiment of the invention,  $X^1$  represents a larger fraction of  $(X^1 + X^2)$ , for example about 0.1 to 1, preferably about 0.3 to 1, and more preferably about 0.35 to 1. In this embodiment, it is a primary objective to maximize the biological effectiveness of the composition, even if this means a relatively low loading of the  
5 exogenous chemical substance has to be accepted.

A significant fraction, for example more than about 10% by weight, preferably more than about 50% by weight, of the amphiphilic salt(s) comprising  $A^+$  cations are believed to be located in the supramolecular aggregates which are colloidally dispersed in the liquid, preferably aqueous, medium of a concentrate liquid composition of the  
10 invention. This can be verified by isolating the supramolecular aggregates from the medium by techniques known in the art such as filtration or centrifugation, and analyzing the two components thus obtained. Upon dilution of a concentrate composition in water to form a plant treatment composition, more of the amphiphilic salt(s) may be partitioned in the aqueous medium; however it is believed that even under these circumstances most or  
15 substantially all of the amphiphilic salt(s) remain in the supramolecular aggregates.

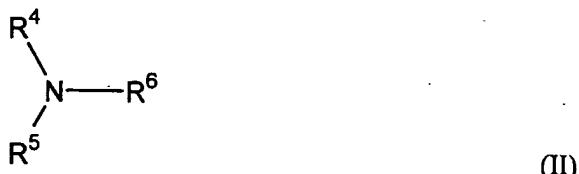
Without being bound by theory, it is believed that location of a significant proportion of an exogenous chemical substance in supramolecular aggregates, as a result of the amphiphilic nature of salt(s) made by neutralizing the exogenous chemical substance with one or more amine compound(s) of formula (I), accounts at least in part for  
20 the superior biological effectiveness of compositions of the invention when applied to foliage of plants, through improved penetration into and through cuticles.

Salt(s) of the second molar amount of the exogenous chemical substance

If a second molar amount of the exogenous chemical substance is present as one or more salt(s) other than a salt comprising  $A^+$  cations, such second molar amount can be  
25 present predominantly in the supramolecular aggregates, predominantly in the aqueous medium, or more or less equally in both. Such salt(s) can be amphiphilic or non-amphiphilic. Where a salt of the second molar amount is an amphiphilic salt, it is believed that it will be predominantly located in the supramolecular aggregates.

The cation(s) of salt(s) of the second molar amount of the exogenous chemical substance are other than those derived from an amine compound of formula (I). Preferred such cations are monovalent cations including (i) alkali metal, for example sodium and  
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potassium, cations, (ii) ammonium cations, (iii) alkylammonium, alkanolammonium and alkanolalkylammonium cations having 1-5 carbon atoms, (iv) alkylsulfonium cations having 1-5 carbon atoms, and (v) cations derived from an amine compound of formula (II):



wherein  $\text{R}^4$  and  $\text{R}^5$  are independently hydrogen, methyl groups or hydrocarbyl chains each having 2 to 5 carbon atoms, and  $\text{R}^6$  is a linear hydrocarbyl chain having 6 to about 22 carbon atoms.  $\text{R}^4$  and  $\text{R}^5$  are preferably independently hydrogen or methyl groups.  $\text{R}^6$  preferably has at least 8, more preferably at least 10 carbon atoms. Preferably  $\text{R}^6$  is 10 derived from lauric, myristic, palmitic, stearic, oleic, linolenic, linoleic and other natural fatty acids, with a saturated  $\text{C}_{12-18}$  chain such as a lauryl, myristyl, palmityl or stearyl group being even more preferred.

Particular examples of cations useful in salts of the second molar amount of the exogenous chemical substance include sodium, ammonium, dimethylammonium, 15 isopropylammonium, monoethanolammonium, trimethylsulfonium, octylammonium, N-lauryl-N,N-dimethylammonium and N-stearyl-N,N-dimethylammonium cations. The last named of these, in its unprotonated form, is available as Noram™ DMSH from CECA S.A.

Cation(s) of salt(s) of the second molar amount of an exogenous chemical 20 substance are sometimes referred to collectively herein as  $\text{B}^+$ . A monobasic salt of glyphosate, or a mixture of monobasic salts of glyphosate, with such cations can therefore be represented by formula (V):



and a dibasic salt or mixture thereof by formula (VI):



For most purposes, even where the exogenous chemical substance is glyphosate, it is preferred that, as in the case of  $\text{A}^+$  cations, the monobasic salt predominate in the composition, in other words, that the amount of all  $\text{B}^+$  cations present be not substantially greater than 1 mole per mole of exogenous chemical substance. At higher mole ratios of

B<sup>+</sup> to exogenous chemical substance, it becomes more difficult to obtain the desired high loading of exogenous chemical substance in a concentrate composition. Thus in a glyphosate composition of the invention where X<sup>2</sup> > 0, it is preferred that, in salt(s) of the second molar amount, salt(s) of formula (V) predominate. For example, it is preferred that  
5 the mole ratio of (V) to (VI) be about 80:20 to 100:0. This corresponds to a mole ratio of B<sup>+</sup> to exogenous chemical substance of about 1:1 to about 1.2:1.

In general, to provide the benefits of the present invention, the amount of B<sup>+</sup> cations present, on a molar basis, should be not greater than about 99% of all cations forming salts with the exogenous chemical substance, i.e., X<sup>2</sup> as a fraction of (X<sup>1</sup> + X<sup>2</sup>) is  
10 0 to about 0.99. It is preferred that the mole ratio of all A<sup>+</sup> and B<sup>+</sup> cations to all exogenous chemical substance anions in the composition be about 1:1 to about 1.2:1.

Optionally, a third molar amount X<sup>3</sup> of the exogenous chemical substance can be present in the form of the acid. Preferably, X<sup>3</sup> is small by comparison with (X<sup>1</sup> + X<sup>2</sup>), for example in a mole ratio of X<sup>3</sup> to (X<sup>1</sup> + X<sup>2</sup>) not greater than about 1:10.

15 Characteristics of a contemplated composition

By selecting the particular amphiphilic salts disclosed herein, the colloidal dispersions of supramolecular aggregates formed, for example when compositions are prepared by a process as described herein, have surprisingly been found to exhibit a high degree of physical stability. The supramolecular aggregates themselves, as well as the  
20 composition as a whole, are physically stable, a feature which is of great benefit in the handling, storage and use of compositions of the invention.

A particularly unexpected discovery is that the supramolecular aggregates substantially maintain their structural integrity even upon dilution to levels useful for direct application to foliage of plants. This structural integrity is not dependent on the  
25 presence of surfactants other than the amphiphilic salt(s) of the exogenous chemical substance (if indeed such amphiphilic salt(s) can be considered "surfactants"). However, as indicated below, surfactants other than the amphiphilic salt(s) of the exogenous chemical substance can optionally be present in compositions of the invention.

More precisely, aqueous concentrate compositions of the invention can be  
30 described as stable colloidal suspensions of supramolecular aggregates. By "stable" in this context it is meant that no phase separation or settling of aggregates occurs during storage

of a composition without agitation at 20-25°C for 48 hours. A stability test is described more fully in the Examples herein. The more desirable aqueous concentrate compositions of the invention are colloidal suspensions in which no phase separation or settling occurs during storage without agitation at constant or varying temperatures from about 10°C to 5 about 40°C for 48 hours, even more desirably from about 0°C to about 50°C for 7 days, and most desirably about -10°C to about 60°C for 30 days. Stability at elevated temperatures for short time periods provides a good indication of long-term stability under normal storage conditions; it is contemplated that certain concentrate compositions of the invention will be stable for periods of 1 year or more under normal storage conditions.

10 The supramolecular aggregates of compositions of the invention are sometimes referred to as nanoparticles. The term "nanoparticle" has no universally accepted definition in the art; however as used herein the term refers to bodies whose longest dimension is of a size up to about 1 µm (1000 nm), and includes bodies that are not solid particulates.

15 In plant treatment compositions of the invention the mean size of the longest dimension of the supramolecular aggregates is about 10 to about 10,000 nm, more preferably about 20 to about 2000 nm, and most preferably about 100 to about 1000 nm. The supramolecular aggregates can be of various shapes, including spherical, cylindrical, needle-like and other shapes. They are often liposome-like in structure. In some 20 compositions of the invention, supramolecular aggregates have been identified as being multilamellar, *i.e.*, having concentric layers like scales of an onion. The mean size of the aggregates can be determined, for example, by light-scattering techniques known in the art. Shapes of aggregates can be determined by observation with an electron microscope.

On dilution in water to a concentration of the exogenous chemical substance of 5 g 25 a.e./l, the colloidal suspension preferably exhibits turbidity corresponding to absorbance of light of wavelength 400 nm of at least 0.5 across a 0.5 cm spectrophotometer cell. A turbidity test is described more fully in the Examples herein.

#### Other optional ingredients

30 Optionally, compositions of the invention can contain agriculturally acceptable materials other than an exogenous chemical substance or a salt thereof as described herein.

For example, more than one exogenous chemical substance can be included. An additional anionic exogenous chemical substance can be included, selected for example

from those hereinbefore listed. Alternatively or in addition, an exogenous chemical substance that is other than anionic as defined herein can be included. For example, a glyphosate composition of the invention can optionally contain, in addition to glyphosate, an anionic herbicidal compound such as acifluorfen, bilanafos, 2,4-D, dicamba, fluazifop, 5 fluoroglycofen, glufosinate, imazapyr, imazaquin, imazethapyr, MCPA, nonanoic acid or picloram. Such additional anionic compound is present as salt(s) comprising A<sup>+</sup>, and optionally B<sup>+</sup>, cations as described herein. Similarly, a composition of the invention containing salts of an anionic herbicide can optionally contain a herbicidal compound that is other than anionic, such as for example an ester derivative of an anionic herbicide, 10 acetochlor, aclonifen, alachlor, atrazine, bensulfuron, bifenox, butachlor, chlorimuron, chlorsulfuron, clomazone, cyanazine, diflufenican, diquat, dithiopyr, diuron, flazasulfuron, flumetsulam, flumioxazin, fluometuron, flupoxam, halosulfuron, isoproturon, isoxaben, metolachlor, metsulfuron, nicosulfuron, oryzalin, oxyfluorfen, paraquat, pendimethalin, phenmedipham, propachlor, propanil, pyridate, sethoxydim, simazine, sulfometuron, 15 thiazopyr, triallate, triasulfuron or trifluralin.

Exogenous chemical substances useful in compositions of the invention can be selected from those listed in standard reference works such as *The Pesticide Manual*, 10th Edition, British Crop Protection Council (1994), and *Farm Chemicals Handbook '97*, Meister Publishing Company (1997).

20 Various agriculturally acceptable adjuvants or excipient substances can also be included, whether or not their purpose is to contribute directly to the biological effectiveness of an exogenous chemical substance in a treated plant. For example, where the exogenous chemical substance is a herbicide, liquid nitrogen fertilizer or ammonium sulfate can be included in the composition. In some instances it can be desirable to include 25 microencapsulated acid in the composition, to lower the pH of a spray solution on contact with foliage.

Other optional components of compositions of the invention include agents to modify color, odor, viscosity, gelling properties, freezing point, stability or texture.

One or more surfactant(s), other than amphiphilic salts of an exogenous chemical 30 substance, can also be included in a contemplated composition. A wide range of surfactants is available to the formulator of exogenous chemical substances and can be selected readily from standard works such as *McCutcheon's Emulsifiers and Detergents*,

1997 Edition, MC Publishing Company, or *Handbook of Industrial Surfactants*, 2nd Edition, Gower (1997).

There is no restriction on the type or chemical class of surfactant that can be used. Nonionic, anionic, cationic and amphoteric types, or combinations of more than one of 5 these types, are all useful in particular situations.

Many surfactants useful herein have a chemical structure that comprises one or more moieties each consisting of a single C<sub>2-4</sub> alkylene oxide unit or a polymerized or copolymerized chain of C<sub>2-4</sub> alkylene oxide units. Such surfactants are referred to as polyoxyalkylene surfactants and include nonionic, anionic, cationic and amphoteric types.

10 Polyoxyalkylene surfactants useful in presently contemplated compositions contain about 2 to about 100 C<sub>2-4</sub> alkylene oxide units. In preferred polyoxyalkylene surfactants the alkylene oxide units form one or more chain(s) of either ethylene oxide or copolymerized ethylene oxide and propylene oxide, each chain of alkylene oxide units having a terminal hydrogen or a C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkanoyl end-cap.

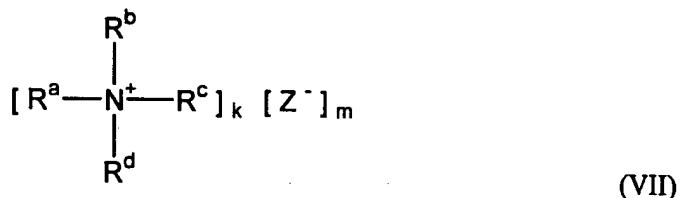
15 Hydrophobic moieties of surfactants useful in compositions of the invention can be essentially hydrocarbon-based, in which case the hydrophobic moieties are typically C<sub>8-24</sub>, preferably C<sub>12-18</sub>, alkyl, alkenyl, alkylaryl, alkanoyl or alkenoyl chains. These chains can be linear or branched. Alternatively, the hydrophobic moieties can contain silicon atoms, for example in the form of siloxane groups such as heptamethyltrisiloxane groups, or 20 fluorine atoms, for example as partially fluorinated alkyl or perfluoroalkyl chains.

Among nonionic surfactants, especially preferred classes include polyoxyethylene alkyl, alkenyl or alkylaryl ethers, such as polyoxyethylene primary or secondary alcohols, alkylphenols or acetylenic diols; polyoxyethylene alkyl or alkenyl esters, such as ethoxylated fatty acids; sorbitan alkylesters, whether ethoxylated or not; glyceryl 25 alkylesters; sucrose esters; and alkyl polyglycosides. Representative specific examples of such nonionic surfactants include polyoxyethylene (9) nonylphenol, Neodol™ 25-7 of Shell (a polyoxyethylene (7) C<sub>12-15</sub> linear primary alcohol), Tergitol™ 15-S-9 of Union Carbide (a polyoxyethylene (9) C<sub>12-15</sub> secondary alcohol), Tween™ 20 of ICI (a polyoxyethylene (20) sorbitan monolaurate), Surfynol™ 465 of Air Products (a 30 polyoxyethylene (10) 2,4,7,9-tetramethyl-5-decyne-4,7-diol) and Agrimul™ PG-2069 of Henkel (a C<sub>9-11</sub> alkyl polyglucoside).

Among anionic surfactants, especially preferred classes include fatty acids, sulfates, sulfonates, and phosphate mono- and diesters of alcohols, alkylphenols, polyoxyethylene alcohols and polyoxyethylene alkylphenols, and carboxylates of polyoxyethylene alcohols and polyoxyethylene alkylphenols. These can be used in their acid form but are more typically used as salts, for example sodium, potassium or ammonium salts.

Among cationic surfactants, especially preferred classes include polyoxyethylene tertiary alkylamines or alkenylamines, such as ethoxylated fatty amines, quaternary ammonium surfactants and polyoxyethylene alkyletheramines. Representative specific examples of such cationic surfactants include polyoxyethylene (5) cocoamine, polyoxyethylene (15) tallowamine, distearyldimethylammonium chloride, N-dodecylpyridine chloride and polyoxypropylene (8) ethoxytrimethylammonium chloride. Particularly preferred polyoxyethylene alkyletheramines are those disclosed in International Publication No. WO 96/32839.

Many cationic quaternary ammonium surfactants of diverse structures are known in the art to be useful in combination with glyphosate and other exogenous chemical substances and can be used in compositions contemplated herein; such quaternary ammonium surfactants have formula (VII):



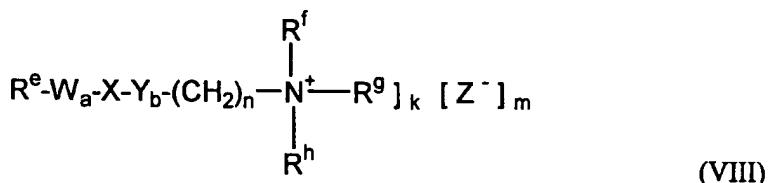
where  $Z^-$  is a suitable anion such as chloride, bromide, iodide, acetate, salicylate, sulfate or phosphate; k and m are integers such that the positive electrical charges on cations balance the negative electrical charges on anions; and options for  $R^a$ ,  $R^b$ ,  $R^c$  and  $R^d$  include, without limitation:

- (i)  $R^a$  is a benzyl or  $C_{8-24}$ , preferably a  $C_{12-18}$ , alkyl or alkenyl group, and  $R^b$ ,  $R^c$  and  $R^d$  are independently  $C_{1-4}$  alkyl, preferably methyl, groups;
- (ii)  $R^a$  and  $R^b$  are independently  $C_{8-24}$ , preferably  $C_{12-18}$ , alkyl or alkenyl groups, and  $R^c$  and  $R^d$  are independently  $C_{1-4}$  alkyl, preferably methyl, groups;
- (iii)  $R^a$  is a  $C_{8-24}$ , preferably a  $C_{12-18}$ , alkyl or alkenyl group,  $R^b$  is a

polyoxyalkylene chain having about 2 to about 100 C<sub>2-4</sub> alkylene oxide units, preferably ethylene oxide units, and R<sup>c</sup> and R<sup>d</sup> are independently C<sub>1-4</sub> alkyl, preferably methyl, groups;

- 5 (iv) R<sup>a</sup> is a C<sub>8-24</sub>, preferably a C<sub>12-18</sub>, alkyl or alkenyl group, R<sup>b</sup> and R<sup>c</sup> are polyoxyalkylene chains having in total about 2 to about 100 C<sub>2-4</sub> alkylene oxide units, preferably ethylene oxide units, and R<sup>d</sup> is a C<sub>1-4</sub> alkyl, preferably a methyl, group; or
- 10 (v) R<sup>a</sup> is a polyoxyalkylene chain having about 2 to about 100 C<sub>2-4</sub> alkylene oxide units in which C<sub>3-4</sub> alkylene oxide units, preferably propylene oxide units, predominate, and R<sup>b</sup>, R<sup>c</sup> and R<sup>d</sup> are independently C<sub>1-4</sub> alkyl, preferably methyl or ethyl, groups. Particularly preferred quaternary ammonium surfactants of this type are those disclosed in U.S. Patent No. 5,464,807.

In a preferred embodiment of the present invention, an amphiphilic quaternary ammonium compound, or mixture of such compounds, is present, having formula (VIII):



15

wherein R<sup>e</sup> is a hydrocarbyl or haloalkyl group having about 6 to about 22 carbon atoms; W and Y are independently O or NH; a and b are independently 0 or 1 but at least one of a and b is 1; X is CO, SO or SO<sub>2</sub>; n is 2 to 4; R<sup>f</sup>, R<sup>g</sup> and R<sup>h</sup> are independently C<sub>1-4</sub> alkyl; and k, m and Z<sup>-</sup> have the same meanings as in formula (VII). R<sup>e</sup> in one particular embodiment is a hydrocarbyl group having about 12 to about 18 carbon atoms. R<sup>e</sup> can also be fluorinated. In one specific embodiment, R<sup>e</sup> is perfluorinated, and preferably has about 6 to about 12 carbon atoms. In one particularly preferred embodiment, R<sup>e</sup> is a saturated perfluoroalkyl group having about 6 to about 12 carbon atoms, X is CO or SO<sub>2</sub>, Y is NH, a is 0, b is 1, n is 3, R<sup>f</sup>, R<sup>g</sup> and R<sup>h</sup> are methyl groups, k and m are each 1, and Z<sup>-</sup> is a chloride, bromide or iodide anion.

Sulfonylamino compounds of formula (VIII), i.e., those wherein X is SO<sub>2</sub>, Y is NH, a is 0 and b is 1, are especially preferred. Suitable examples include 3-(((heptadecafluoroctyl)sulfonyl)amino)-N,N,N-trimethyl-1-propaminium iodide, available for example as Fluorad™ FC-135 from 3M Company, and the corresponding

chloride. It is believed that Fluorad™ FC-754 of 3M Company comprises the corresponding chloride.

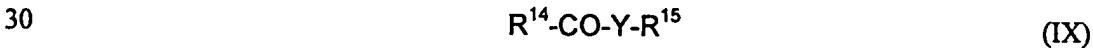
When included, amphiphilic quaternary ammonium compound(s) of formula (VIII) are present in an adjuvant amount, *i.e.*, an amount sufficient to provide visibly improved 5 biological effectiveness of the exogenous chemical substance by comparison with a composition lacking such compound(s). "Visibly improved" in the present context means that, in a side-by-side comparison, a difference in biological effectiveness in favor of the composition containing the amphiphilic quaternary ammonium compound(s) would be evident to an experienced technician in the art relating to the particular class of exogenous 10 chemical substance being applied, for example a weed scientist in the case where the exogenous chemical substance is a herbicide.

When present, one or more amphiphilic quaternary ammonium compound(s) of formula (VIII) are preferably included in a ratio of total weight of such compound(s) to weight of the anionic exogenous chemical substance, expressed as acid equivalent, of 15 about 1:3 to about 1:100.

Suitable concentrations of a compound of formula (VIII) are about 0.001% to about 1% by weight in a plant treatment composition, and about 0.01% to about 10% by weight in a liquid concentrate composition of the invention.

Yet another class of excipient material that can be useful in compositions of the 20 present invention is an oil, such as a triglyceride ester of fatty acids of animal, vegetable or synthetic origin, a paraffin, a polysiloxane, or a fatty acid or an ester or amide thereof. Such an oil, or mixture of oils, is present in an adjuvant amount as defined above. Examples of suitable oils include triglyceride esters of the coconut oil type, such as the product Miglyol™ 812 of Hüls, corn oil, olive oil, C<sub>12-15</sub> alkyl benzoate, eicosapentaenoic 25 and docosahexaenoic acids and alkyl and triglyceride esters thereof and triglyceride ester of caprylic acid. Oils can be fractionated or not. Fractionation permits elimination of certain fatty acid chain lengths so as to modify melting point.

In a particular embodiment of the invention, one or more oil(s) are included, each having a chemical structure corresponding to formula (IX):



wherein R<sup>14</sup> is a hydrocarbyl group having about 5 to about 21 carbon atoms, R<sup>15</sup> is a hydrocarbyl group having 1 to about 14 carbon atoms, the total number of carbon atoms in

R<sup>14</sup> and R<sup>15</sup> is about 11 to about 27, and Y is O or NH. R<sup>14</sup> and R<sup>15</sup> are preferably linear hydrocarbyl chains. R<sup>14</sup> preferably has about 11 to about 21 carbon atoms and is preferably derived from a natural saturated or unsaturated fatty acid. R<sup>15</sup> is preferably an alkyl group with 1 to about 6 carbon atoms. Especially preferred oils of formula (IX) are therefore C<sub>1-6</sub> alkylesters or C<sub>1-6</sub> alkylamides of fatty acids. It is further preferred that R<sup>14</sup> is saturated in about 40% to 100% by weight of all compounds of formula (IX) present in the composition.

In certain preferred embodiments, an oil is included that is a C<sub>1-4</sub> alkylester of a C<sub>12-18</sub> fatty acid, more preferably a C<sub>1-4</sub> alkylester of a C<sub>12-18</sub> saturated fatty acid. Examples include methyl oleate, ethyl oleate, isopropyl myristate, isopropyl palmitate and butyl stearate. Butyl stearate is especially preferred.

When present, one or more oil(s) of formula (IX) are preferably included in a ratio of total weight of such oil(s) to weight of the cationic exogenous chemical substance, expressed as acid equivalent, of about 1:3 to about 1:100.

Suitable concentrations of an oil of formula (IX) are about 0.001% to about 1% by weight in a plant treatment composition, and about 0.01% to about 10% by weight in a liquid concentrate composition of the invention.

Oil(s), if present, can be emulsified in a composition of the invention by means of the amphiphilic salt(s) of the exogenous chemical substance. If desired, additional surfactant(s) can be included as emulsifier(s) for such oil(s). It is believed that the presence of oil, especially an oil of formula (IX), in the composition can further enhance penetration of the exogenous chemical substance into or through plant cuticles, perhaps as a result of the more lipophilic character imparted to the composition.

#### Process for making a composition of the invention

Liquid concentrate compositions in accordance with the present invention can be prepared by the following general procedure; however, the invention is not limited to compositions made by this procedure.

In a suitable process, the first step is a neutralizing step. This step comprises neutralization of a first molar amount X<sup>1</sup> of an anionic exogenous chemical substance with one or more amine compound(s) of formula (I) in a liquid medium, preferably an aqueous medium, with agitation to make a liquid composition containing one or more amphiphilic salt(s) of the exogenous chemical substance. In an example of the neutralizing step where

the exogenous chemical substance is glyphosate, a first molar amount  $X^1$  of glyphosate acid ( $GH_2$ ) is added to water together with an amine compound of formula (I), in an amount of about 1 to about 2 moles per mole of glyphosate, to make a monobasic salt  $[GH^-][A^+]$ , a dibasic salt  $[G^{2-}][A^+]_2$ , or a mixture of such monobasic and dibasic salts, 5 where  $A^+$  is a cation derived by protonation of the amine compound. The relative molar proportions of monobasic and dibasic salts is a function of the quantity of the amine compound added per mole of glyphosate.

Optionally the neutralizing step further comprises introducing to the liquid composition, with agitation, a second molar amount  $X^2$  of the exogenous chemical 10 substance in the form of one or more salt(s) other than an amphiphilic salt formed by neutralizing the exogenous chemical substance with an amine compound of formula (I).  $X^1$  as a fraction of  $(X^1 + X^2)$  is in a range of about 0.01 to 1. In an example of this optional introduction as part of the neutralizing step where the exogenous chemical substance is glyphosate, a second molar amount  $X^2$  of glyphosate is added in the form of a 15 monobasic salt  $[GH^-][B^+]$ , a dibasic salt  $[G^{2-}][B^+]_2$ , or a mixture of such monobasic and dibasic salts, where  $B^+$  is a cation derived from a base other than an amine compound of formula (I).

The salt(s) of the second molar amount of the exogenous chemical substance can 20 be prepared separately in advance, or made *in situ* by neutralizing, in the liquid medium with agitation, this second molar amount with one or more base(s) other than an amine compound of formula (I). In either case, introduction of such salt(s) can occur before, during or after neutralization of the first molar amount of the exogenous chemical substance.

The neutralizing step takes place with agitation, preferably moderate agitation, for 25 example using a magnetic stirrer. In a preferred embodiment, the neutralizing step is conducted at a temperature higher than the melting point of the amine compound(s) of formula (I) used. Typically the temperature of the liquid medium during the neutralizing step is about 50°C to about 100°C.

In a suitable process, the second step is a conditioning step. This step comprises 30 continuing the agitation of the liquid composition until supramolecular aggregates comprising amphiphilic salt(s) of the exogenous chemical substance formed by neutralizing the exogenous chemical substance with an amine compound of formula (I) are

colloidally dispersed in the liquid medium. Agitation, preferably moderate agitation, can be provided, for example, by the same device used to agitate during the neutralizing step. It is preferred to maintain an elevated temperature, similar to that provided during the neutralizing step, throughout the conditioning step. The conditioning step typically lasts 5 for a period of a few minutes to a few hours and results in spontaneous formation of a stable colloidal suspension of supramolecular aggregates.

Optional ingredients other than salt(s) of the exogenous chemical substance can be dissolved or dispersed in the liquid medium prior to, during or after the neutralization step and prior to, during or after the conditioning step. An optimum order of addition can 10 readily be established for any composition by routine experimentation.

Application of a contemplated composition to foliage

Exogenous chemical substances should be applied to plants at a rate sufficient to give the desired effect. These application rates are usually expressed as amount of exogenous chemical substance per unit area treated, e.g. grams per hectare (g/ha). What 15 constitutes a "desired effect" varies according to the standards and practice of those who investigate, develop, market and use a specific class of exogenous chemicals. For example, in the case of a herbicide, the amount applied per unit area to give 85% control of a plant species as measured by growth reduction or mortality is often used to define a commercially effective rate.

20 Herbicidal effectiveness is one of the biological effects that can be enhanced through this invention. "Herbicidal effectiveness," as used herein, refers to any observable measure of control of plant growth, which can include one or more of the actions of (1) killing, (2) inhibiting growth, reproduction or proliferation, and (3) removing, destroying, or otherwise diminishing the occurrence and activity of plants.

25 The selection of application rates that are biologically effective for a specific exogenous chemical substance is within the skill of the ordinary agricultural scientist. Those of skill in the art will likewise recognize that individual plant conditions, weather and growing conditions, as well as the specific exogenous chemical substance and composition thereof selected, will influence the degree of biological effectiveness 30 achieved in practicing this invention. Useful application rates for exogenous chemical substances employed can depend upon all of the above conditions. With respect to the use of the method of this invention for glyphosate herbicide, much information is known about

appropriate application rates. Over two decades of glyphosate use and published studies relating to such use have provided abundant information from which a weed control practitioner can select glyphosate application rates that are herbicidally effective on particular species at particular growth stages in particular environmental conditions.

5       Herbicidal compositions of glyphosate or derivatives thereof are used to control a very wide variety of plants worldwide. Glyphosate compositions of the invention can be applied to a plant in a herbicidally effective amount, and can effectively control one or more plant species of one or more of the following genera without restriction: *Abutilon*, *Amaranthus*, *Artemisia*, *Asclepias*, *Avena*, *Axonopus*, *Borreria*, *Brachiaria*, *Brassica*,  
10     *Bromus*, *Chenopodium*, *Cirsium*, *Commelina*, *Convolvulus*, *Cynodon*, *Cyperus*, *Digitaria*,  
*Echinochloa*, *Eleusine*, *Elymus*, *Equisetum*, *Erodium*, *Helianthus*, *Imperata*, *Ipomoea*,  
*Kochia*, *Lolium*, *Malva*, *Oryza*, *Ottochloa*, *Panicum*, *Paspalum*, *Phalaris*, *Phragmites*,  
*Polygonum*, *Portulaca*, *Pteridium*, *Pueraria*, *Rubus*, *Salsola*, *Setaria*, *Sida*, *Sinapis*,  
*Sorghum*, *Triticum*, *Typha*, *Ulex*, *Xanthium* and *Zea*.

15     Particularly important annual broadleaf species for which glyphosate compositions are used are exemplified without limitation by the following: velvetleaf (*Abutilon theophrasti*), pigweed (*Amaranthus* spp.), buttonweed (*Borreria* spp.), oilseed rape, canola, indian mustard, etc. (*Brassica* spp.), commelina (*Commelina* spp.), filaree (*Erodium* spp.), sunflower (*Helianthus* spp.), morningglory (*Ipomoea* spp.), kochia  
20     (*Kochia scoparia*), mallow (*Malva* spp.), wild buckwheat, smartweed, etc. (*Polygonum* spp.), purslane (*Portulaca* spp.), russian thistle (*Salsola* spp.), sida (*Sida* spp.), wild mustard (*Sinapis arvensis*) and cocklebur (*Xanthium* spp.)

Particularly important annual narrowleaf species for which glyphosate compositions are used are exemplified without limitation by the following: wild oat  
25     (*Avena fatua*), carpetgrass (*Axonopus* spp.), downy brome (*Bromus tectorum*), crabgrass (*Digitaria* spp.), barnyardgrass (*Echinochloa crus-galli*), goosegrass (*Eleusine indica*), annual ryegrass (*Lolium multiflorum*), rice (*Oryza sativa*), ottochloa (*Ottochloa nodosa*), bahiagrass (*Paspalum notatum*), canarygrass (*Phalaris* spp.), foxtail (*Setaria* spp.), wheat (*Triticum aestivum*) and corn (*Zea mays*).

30     Particularly important perennial broadleaf species for which glyphosate compositions are used are exemplified without limitation by the following: mugwort

(*Artemesia* spp.), milkweed (*Asclepias* spp.), canada thistle (*Cirsium arvense*), field bindweed (*Convolvulus arvensis*) and kudzu (*Pueraria* spp.).

Particularly important perennial narrowleaf species for which glyphosate compositions are used are exemplified without limitation by the following: brachiaria  
5 (*Brachiaria* spp.), bermudagrass (*Cynodon dactylon*), yellow nutsedge (*Cyperus esculentus*), purple nutsedge (*C. rotundus*), quackgrass (*Elymus repens*), lalang (*Imperata cylindrica*), perennial ryegrass (*Lolium perenne*), guineagrass (*Panicum maximum*), dallisgrass (*Paspalum dilatatum*), reed (*Phragmites* spp.), johnsongrass (*Sorghum halepense*) and cattail (*Typha* spp.).

10 Other particularly important perennial species for which glyphosate compositions are used are exemplified without limitation by the following: horsetail (*Equisetum* spp.), bracken (*Pteridium aquilinum*), blackberry (*Rubus* spp.) and gorse (*Ulex europaeus*).

Thus, glyphosate compositions of the present invention, and a process for treating plants with such compositions, can be useful on any of the above species. In a particular  
15 contemplated process, a plant treatment composition of the invention comprising one or more amphiphilic glyphosate salt(s) of formula (III) or (IV) is applied to foliage of crop plants genetically transformed to tolerate glyphosate, and simultaneously to foliage of weeds or undesired plants growing in close proximity to such crop plants. This process results in control of the weeds or undesired plants while leaving the crop plants  
20 substantially unharmed. Crop plants genetically transformed to tolerate glyphosate include those whose seeds are sold by Monsanto or under license from Monsanto bearing the Roundup Ready® trademark. These include varieties of cotton, soybean, canola and corn.

Application of plant treatment compositions to foliage of plants is preferably  
25 accomplished by spraying, using any conventional means for spraying liquids, such as spray nozzles, atomizers, or the like. Compositions of the present invention can be used in precision farming techniques, in which apparatus is employed to vary the amount of exogenous chemical substance applied to different parts of a field, depending on variables such as the particular plant species present, soil composition, and the like. In one  
30 embodiment of such techniques, a global positioning system operated with the spraying apparatus can be used to apply the desired amount of the composition to different parts of a field.

A plant treatment composition is preferably dilute enough to be readily sprayed using standard agricultural spray equipment. Suitable application rates for the present invention vary depending upon a number of factors, including the type and concentration of active ingredient and the plant species involved. Useful rates for applying an aqueous 5 composition to a field of foliage can range from about 25 to about 1,000 liters per hectare (l/ha), preferably about 50 to about 300 l/ha, by spray application.

A contemplated process for eliciting a desired biological activity in a plant or in a pathogen, parasite or feeding organism present in or on a plant further comprises, prior to the step of applying a plant treatment composition of the invention to foliage of the plant, 10 a step of diluting, in a suitable volume of water, a liquid concentrate composition as provided herein to form the plant treatment composition.

#### EXAMPLES

The following Examples are provided for illustrative purposes only and are not intended to limit the scope of the present invention. The Examples will permit better 15 understanding of the invention and perception of its advantages and certain variations of execution.

##### Example 1

Glyphosate acid, in the form of a wet cake having a glyphosate assay of 86.5% a.e. by weight, is introduced in an amount of 0.47 g (equivalent to 2.4 mmol GH<sub>2</sub>) to a 30 ml 20 flask. N,N-distearyl-N-methylamine (Noram™ M2SH of CECA S.A.) is then added in the amount of 1.24 g, calculated to be equivalent to 2.4 mmol to provide an amine to glyphosate a.e. mole ratio of 1:1. Next, 20 ml of deionized water (ion-exchanged and passed through a 0.2 µm filter) is added to provide an aqueous medium for neutralization of the glyphosate with the N,N-distearyl-N-methylamine.

25 The flask is stoppered and placed in a water bath at 60°C for 2 hours. Magnetic agitation is applied to ensure thorough mixing.

A stable colloidal suspension is obtained which is of low viscosity and has a pH of about 4. The colloidal suspension is characterized by the following procedures.

- Stability of the colloidal suspension is determined by observation. If no phase separation appears in the preparation flask upon storage for 48 hours without

agitation, at ambient temperature, the colloidal suspension is considered stable for purposes of the present Example.

- Turbidity of the colloidal suspension, after dilution to a glyphosate concentration of 5 g a.e./l, is measured by means of a UV/visible spectrophotometer, model Lambda<sub>2</sub><sup>TM</sup> of Perkin Elmer, at a wavelength of 400 nm. Spectrophotometer cells 0.5 cm in width are used. Turbidity is given by absorbance recorded per centimeter path length of light (abs/cm), i.e., in this case absorbance divided by 0.5.
- Size of the colloidal particles (supramolecular aggregates) is measured by light-scattering after dilution to a glyphosate concentration of 50 mg a.e./l. A Brookhaven apparatus is used. Size of the colloidal particles can also be observed by transmission electron microscopy (TEM) using the negative staining technique. The colorant used is sodium silicotungstate, Na<sub>4</sub>(Si(W<sub>3</sub>O<sub>10</sub>)<sub>4</sub>).20H<sub>2</sub>O. A transmission electron micrograph showing supramolecular aggregates is presented in Figure 1.

Results for Example 1 are presented in Table 1 below.

#### Example 2

The procedure of Example 1 is followed, except that the amine compound used is N,N-dilauryl-N-methylamine (Noram<sup>TM</sup> M2C of CECA S.A.). The weight of amine introduced is 0.83 g. Results for Example 2 are presented in Table 1 below.

#### Example 3

The procedure of Example 1 is followed, except that the amine compound used is dilaurylamine (Noram<sup>TM</sup> 2C of CECA S.A.). The weight of amine introduced is 0.79 g. Results for Example 3 are presented in Table 1 below.

#### Example 4

The procedure of Example 1 is followed, except that the amine compound is added in an amine to glyphosate a.e. mole ratio of 2:1. The amine compound is N,N-distearyl-N-methylamine (Noram<sup>TM</sup> M2SH). The weight of amine introduced is 2.48 g. A stable colloidal suspension is obtained having a pH of about 7. Results for Example 4 are presented in Table 1 below.

Example 5

The procedure of Example 4 is followed, except that the amine compound is N,N-dilauryl-N-methylamine (Noram™ M2C). The weight of amine introduced is 1.66 g. Results for Example 5 are presented in Table 1 below.

5 Example 6

The procedure of Example 4 is followed, except that the amine compound is dilaurylamine (Noram™ 2C). The weight of amine introduced is 1.58 g. Results for Example 6 are presented in Table 1 below.

Table 1: Results for Examples 1-6

Example	Amine compound <sup>1</sup>	Mole ratio <sup>2</sup>	Appearance	Turbidity (abs/cm)	Phase separation	Average size of aggregates (nm)
1	2C <sub>18</sub> -NMe	1:1	milky white	3	no	200
2	2C <sub>12</sub> -NMe	1:1	bluish white	1	no	101
3	2C <sub>12</sub> -NH	1:1	bluish white	4	no	165
4	2C <sub>18</sub> -NMe	2:1	milky white	4	no	380
5	2C <sub>12</sub> -NMe	2:1	milky white	>5	no	200
6	2C <sub>12</sub> -NH	2:1	milky white	>5	no	170

10 <sup>1</sup> amine compound of formula (I); abbreviations for amine compounds can be understood by reference to the Examples.

<sup>2</sup> mole ratio of amine compound of formula (I) to glyphosate a.e.

Example 7a

Glyphosate acid, in the form of a wet cake having a glyphosate assay of 86.5% a.e. 15 by weight, is introduced in an amount of 0.47 g (equivalent to 2.4 mmol GH<sub>2</sub>) to a 30 ml flask. N,N-distearyl-N-methylamine (Noram™ M2SH of CECA S.A.) is then added in the amount of 0.43 g, calculated to be equivalent to 0.84 mmol to provide an N,N-distearyl-N-methylamine to glyphosate a.e. mole ratio of 0.35:1. Next, 20 ml of deionized water (ion-exchanged and passed through a 0.2 µm filter) is added to provide an aqueous medium for 20 partial neutralization of the glyphosate with the N,N-distearyl-N-methylamine.

The flask is stoppered and placed in a water bath at 60°C for 2 hours. Magnetic agitation is applied to ensure thorough mixing. Octylamine is then added in the amount of 0.20 g, calculated to be equivalent to 1.56 mmol to provide an octylamine to glyphosate

a.e. mole ratio of 0.65:1 and a total base to glyphosate a.e. mole ratio of 1:1. The flask is left in the water bath for 30 minutes while agitation is maintained.

A stable colloidal suspension is obtained which is of low viscosity and has a pH of about 4. The colloidal suspension is characterized by the procedures of Example 1.

5 Results for Example 7a are presented in Table 2 below.

#### Example 7b

The procedure of Example 7a is followed, except that the amount of N,N-distearyl-N-methylamine added is 0.62 g, calculated to be equivalent to 1.2 mmol to provide an N,N-distearyl-N-methylamine to glyphosate a.e. mole ratio of 0.5:1; and the amount of 10 octylamine added is 0.155 g, calculated to be equivalent to 1.2 mmol to provide an octylamine to glyphosate a.e. mole ratio of 0.5:1 and a total base to glyphosate a.e. mole ratio of 1:1. Results for Example 7b are presented in Table 2 below.

#### Example 7c

The procedure of Example 7a is followed, except that the amount of N,N-distearyl-N-methylamine added is 0.99 g, calculated to be equivalent to 1.92 mmol to provide an N,N-distearyl-N-methylamine to glyphosate a.e. mole ratio of 0.8:1; and the amount of octylamine added is 0.062 g, calculated to be equivalent to 0.48 mmol to provide an octylamine to glyphosate a.e. mole ratio of 0.2:1 and a total base to glyphosate a.e. mole ratio of 1:1. Results for Example 7c are presented in Table 2 below.

20 Example 8

Glyphosate acid, in the form of a wet cake having a glyphosate assay of 86.5% a.e. by weight, is introduced in an amount of 0.47 g (equivalent to 2.4 mmol GH<sub>2</sub>) to a 30 ml flask. N,N-distearyl-N-methylamine (Noram™ M2SH of CECA S.A.) is then added in the amount of 0.62 g, calculated to be equivalent to 1.2 mmol to provide an N,N-distearyl-N-methylamine to glyphosate a.e. mole ratio of 0.5:1. Next, 20 ml of deionized water (ion-exchanged and passed through a 0.2 µm filter) is added to provide an aqueous medium for partial neutralization of the glyphosate with the N,N-distearyl-N-methylamine.

The flask is stoppered and placed in a water bath at 60°C for 2 hours. Magnetic agitation is applied to ensure thorough mixing. A 1M sodium hydroxide solution is then 30 added in the amount of 1.18 ml, to provide 1.18 mmol sodium hydroxide, giving a sodium

hydroxide to glyphosate a.e. mole ratio of 0.5:1 and a total base to glyphosate a.e. mole ratio of 1:1. The flask is left in the water bath for 30 minutes while agitation is maintained.

A stable colloidal suspension is obtained which is of low viscosity and has a pH of  
5 about 4. The colloidal suspension is characterized by the procedures of Example 1.  
Results for Example 8 are presented in Table 2 below.

Table 2: Results for Examples 7-8

Example	Amine compound <sup>1</sup>	Mole ratio <sup>2</sup>	Appearance	Turbidity (abs/cm)	Phase separation	Average size of aggregates (nm)
7a	2C <sub>18</sub> -NMe	0.35:1	milky white	>5	no	170
7b	2C <sub>18</sub> -NMe	0.5:1	milky white	5	no	110
7c	2C <sub>18</sub> -NMe	0.8:1	turbid white	2	no	100
8	2C <sub>18</sub> -NMe	0.5:1	milky white	>5	no	102

<sup>1</sup> amine compound of formula (I); abbreviations for amine compounds can be understood by reference to the Examples.

10 <sup>2</sup> mole ratio of amine compound of formula (I) to glyphosate a.e.

#### Example 9

Glyphosate acid, in the form of a wet cake having a glyphosate assay of 86.5% a.e. by weight, is introduced in an amount of 0.47 g (equivalent to 2.4 mmol GH<sub>2</sub>) to a 30 ml flask. N,N-distearyl-N-methylamine (Noram™ M2SH of CECA S.A.) is then added in the 15 amount of 1.24 g, calculated to be equivalent to 2.4 mmol to provide an N,N-distearyl-N-methylamine to glyphosate a.e. mole ratio of 1:1. Next, 20 ml of deionized water (ion-exchanged and passed through a 0.2 µm filter) is added to provide an aqueous medium for neutralization of the glyphosate with the N,N-distearyl-N-methylamine.

The flask is stoppered and placed in a water bath at 60°C for 2 hours. Magnetic 20 agitation is applied to ensure thorough mixing. N-stearyl-N,N-dimethylamine (Noram™ DMSH of CECA S.A.) is then added in the amount of 0.71 g, to provide 2.4 mmol N-stearyl-N,N-dimethylamine, giving an N-stearyl-N,N-dimethylamine to glyphosate a.e. mole ratio of 1:1 and a total base to glyphosate a.e. mole ratio of 2:1. The flask is left in the water bath for 30 minutes while agitation is maintained.

A stable colloidal suspension is obtained which is of low viscosity and has a pH of about 4. The colloidal suspension is characterized by the procedures of Example 1. Results for Example 9 are presented in Table 3 below.

Table 3: Results for Example 9

Example	Amine compound <sup>1</sup>	Mole ratio <sup>2</sup>	Appearance	Turbidity (abs/cm)	Phase separation	Average size of aggregates (nm)
9	2C <sub>18</sub> -NMe	1:1	milky white	>5	no	220

5 <sup>1</sup> amine compound of formula (I); abbreviations for amine compounds can be understood by reference to the Examples.

<sup>2</sup> mole ratio of amine compound of formula (I) to glyphosate a.e.

#### Example 10

N,N-distearyl-N-methylamine (Noram™ M2SH) in the amount of 1.24 g and an oil 10 comprising triglyceride ester of fatty acids (Miglyol™ 812 of Hüls) in the amount of 0.62 g are introduced to a 30 ml flask. The flask is stoppered, then placed in a water bath at 60°C, with magnetic agitation, until the amine compound dissolves in the oil. Glyphosate acid, in the form of a wet cake having a glyphosate assay of 86.5% a.e. by weight, is then added in an amount of 470 mg (equivalent to 2.4 mmol GH<sub>2</sub>). Next, 20 ml 15 of deionized water (ion-exchanged and passed through a 0.2 µm filter) is added to provide an aqueous medium for neutralization of the glyphosate with the amine compound.

The flask is stoppered again and placed in a water bath at 60°C for 2 hours. Magnetic agitation is applied to ensure thorough mixing.

A stable colloidal suspension is obtained which is of low viscosity and has a pH of 20 about 4. The colloidal suspension is characterized by the procedures of Example 1. Results for Example 10 are presented in Table 4 below.

#### Example 11

The procedure of Example 10 is followed, except that the amine compound used is N,N-dilauryl-N-methylamine (Noram™ M2C of CECA S.A.). The weight of amine 25 introduced is 0.788 g. The weight of oil introduced is 0.62 g. Results for Example 11 are presented in Table 4 below.

Table 4: Results for Examples 10-11

Example	Amine compound <sup>1</sup>	Mole ratio <sup>2</sup>	Appearance	Turbidity (abs/cm)	Phase separation	Average size of aggregates (nm)
10	2C <sub>18</sub> -NMe	1:1	milky white	4	no	140
11	2C <sub>12</sub> -NMe	1:1	milky white	>5	no	230

<sup>1</sup> amine compound of formula (I); abbreviations for amine compounds can be understood by reference to the Examples.

<sup>2</sup> mole ratio of amine compound to glyphosate a.e.

##### 5 Example 12

Dioctylamine in the amount of 8.76 g, glyphosate acid (assay 96% by weight) in the amount of 11.99 g, and distilled water in the amount of 219.3 g distilled water are introduced to a 500 ml screw-topped vial. The mass fraction of glyphosate introduced is thus 50 grams per kilogram (g/kg). The mixture of ingredients is magnetically stirred at 10 50°C for 3 hours to obtain a turbid colloidal suspension containing supramolecular aggregates. The suspension is cooled to room temperature. The pH of the formulation and the size of supramolecular aggregates (by dynamic light scattering) are measured after dilution of the suspension with distilled water to a glyphosate concentration of 5 g a.e./kg. The 50 g a.e./kg suspension is examined for phase separation after standing without 15 agitation at ambient temperature for 48 hours. Results for Example 12 are presented in Table 5 below.

##### Example 13

The procedure of Example 12 is followed, except that the amine compound is trihexylamine, added in the amount of 19.2 g, glyphosate acid is added in the amount of 20 12.0 g and distilled water is added in the amount of 209 g. Results for Example 13 are presented in Table 5 below.

##### Example 14

The procedure of Example 12 is followed, except that the amine compound is N,N-dioctyl-N-methylamine, added in the amount of 15.2 g, glyphosate acid is added in 25 the amount of 12.0 g and distilled water is added in the amount of 213 g. Results for Example 14 are presented in Table 5 below.

Example 15

The procedure of Example 12 is followed, except that the amine compound is didecylamine, added in the amount of 21.4 g, glyphosate acid is added in the amount of 8.8 g and distilled water is added in the amount of 195 g. Glyphosate concentration in the suspension is 39 g a.e./kg. Results for Example 15 are presented in Table 5 below.

Example 16

The procedure of Example 12 is followed, except that the amine compound is dilaurylamine (Noram™ 2C), added in the amount of 36.0 g, glyphosate acid is added in the amount of 12.0 g and distilled water is added in the amount of 192 g. Results for Example 16 are presented in Table 5 below.

Example 17

The procedure of Example 12 is followed, except that the amine compound is N,N-dilauryl-N-methylamine (Noram™ M2C), added in the amount of 28.0 g, glyphosate acid is added in the amount of 10.0 g and distilled water is added in the amount of 175 g. Glyphosate concentration in the suspension is 47 g a.e./kg. Results for Example 17 are presented in Table 5 below.

Example 18

The procedure of Example 12 is followed, except that the amine compound is N,N-distearyl-N-methylamine (Noram™ M2SH), added in the amount of 52.0 g, glyphosate acid is added in the amount of 12.0 g and distilled water is added in the amount of 176 g. Results for Example 18 are presented in Table 5 below.

Table 5: Results for Examples 12-18

Example	Amine compound <sup>1</sup>	Mole ratio <sup>2</sup>	Appearance	pH	Phase separation	Average size of aggregates (nm)
12	2C <sub>8</sub> -NH	1:1	not recorded	3.2	no	100
13	3C <sub>6</sub> -N	1:1	clear, golden	4.6	no	8 and 130
14	2C <sub>8</sub> -NMe	1:1	clear, colorless	4.0	no	90
15	2C <sub>10</sub> -NH	1:1	milky white	3.0	no	137
16	2C <sub>12</sub> -NH	1:1	milky	3.0	no	403
17	2C <sub>12</sub> -NMe	1:1	opaque, milky	3.2	no	60
18	2C <sub>18</sub> -NMe	1:1	opaque gel	3.2	no	160

<sup>1</sup> amine compound of formula (I); abbreviations for amine compounds can be understood by reference to the Examples.

<sup>2</sup> mole ratio of amine compound of formula (I) to glyphosate a.e.

#### Example 19

5 N,N-distearyl-N-methylamine (Noram™ M2SH) in the amount of 37.5 g and glyphosate acid (assay 96% by weight) in the amount of 12.0 g are introduced to a 500 ml screw-topped vial. Next, 12.0 g of isopropanol and 12 g of n-butanol are added, followed by 218 g of distilled water. The mass fraction of glyphosate introduced is thus 50 grams per kilogram (g/kg). The mixture of ingredients is magnetically stirred at 50°C for 5 hours  
 10 to obtain a turbid colloidal suspension containing supramolecular aggregates. The suspension is cooled to room temperature. The pH of the formulation and the size of supramolecular aggregates (by dynamic light scattering) are measured after dilution of the suspension with distilled water to a glyphosate concentration of 5 g a.e./kg. Results for Example 19 are presented in Table 6 below.

15

Table 6: Results for Example 19

Example	Amine compound <sup>1</sup>	Mole ratio <sup>2</sup>	Appearance	pH	Phase separation	Average size of aggregates (nm)
19	2C <sub>18</sub> -NMe	1:1	not recorded	3.0	no	460

<sup>1</sup> amine compound of formula (I); abbreviations for amine compounds can be understood by reference to the Examples.

<sup>2</sup> mole ratio of amine compound of formula (I) to glyphosate a.e.

#### Example 20

20 The composition of Example 19 (comprising mono(N,N-distearyl-N-methylammonium) glyphosate formulated with isopropanol and n-butanol as described above) is evaluated for herbicidal effectiveness in a greenhouse test by foliar application to a representative annual broadleaf species, velvetleaf (*Abutilon theophrasti*, ABUTH) and a representative annual narrowleaf species, Japanese millet, a form of barnyardgrass  
 25 (*Echinochloa crus-galli*, ECHCF). For comparative purposes, the following commercial standard formulations were included in the test:

- MON 0139, an aqueous solution of the mono(isopropylammonium) salt of glyphosate, containing 62% by weight of said salt and no other formulation ingredients except water, available from Monsanto Company; and
- Roundup® Ultra herbicide, an aqueous solution concentrate formulation of the mono(isopropylammonium) salt of glyphosate, containing 41% by weight of said salt together with a surfactant, this product being sold as an agricultural herbicide by Monsanto Company in the U.S.A.

MON 0139 contains glyphosate at a concentration of about 680 grams of acid equivalent per liter (g a.e./l) and Roundup® Ultra herbicide contains 356 g a.e./l.

10 The following procedure is used for the greenhouse test.

Seeds of the plant species indicated are planted in 85 mm square pots in a soil mix which has previously been steam sterilized and prefertilized with a 14-14-14 NPK slow release fertilizer at a rate of 3.6 kg/m<sup>3</sup>. The pots are placed in a greenhouse with sub-irrigation. About one week after emergence, seedlings are thinned as needed, including  
15 removal of any unhealthy or abnormal plants, to create a uniform series of test pots.

The plants are maintained for the duration of the test in the greenhouse where they receive a minimum of 14 hours of light per day. If natural light is insufficient to achieve the daily requirement, artificial light with an intensity of approximately 475 microeinsteins is used to make up the difference. Exposure temperatures are not precisely controlled but  
20 average about 27°C during the day and about 18°C during the night. Plants are sub-irrigated throughout the test to ensure adequate soil moisture levels. Relative humidity is maintained at about 50% for the duration of the test.

Pots are assigned to different treatments in a fully randomized experimental design with 3 replications. A set of pots is left untreated as a reference against which effects of  
25 the treatments can later be evaluated. Two sets of 3 replications are provided for treatments with Roundup® Ultra, to ensure a sound basis is available for comparison of herbicidal effectiveness of compositions of the invention.

Application of glyphosate compositions to foliage is made by spraying with a track sprayer fitted with a TeeJet™ 9501E nozzle calibrated to deliver a spray volume of 93  
30 liters per hectare (l/ha) at a pressure of 166 kilopascals (kPa). Application is made when the plants are 2-3 weeks old. After treatment, pots are returned to the greenhouse until ready for evaluation, in this Example 15 days after treatment (DAT).

Treatments are made using dilute aqueous compositions, prepared by dilution with water of preformulated concentrate compositions. All comparisons are made at equal glyphosate acid equivalent rates. The required degree of dilution for a glyphosate concentrate composition to make a plant treatment composition is calculated from the  
 5 equation

$$A = RS/VC$$

where A is the volume in milliliters (ml) of the glyphosate composition to be added to the plant treatment composition being prepared, R is the desired glyphosate rate in grams of acid equivalent per hectare (g a.e./ha), S is the total volume in milliliters (ml) of plant  
 10 treatment composition being prepared, V is the application rate in liters per hectare (l/ha) of plant treatment composition, conventionally referred to as "spray volume", and C is the concentration of glyphosate in grams of acid equivalent per liter (g a.e./l) in the glyphosate composition.

For evaluation of herbicidal effectiveness, all plants in the test are examined by a  
 15 single practiced technician, who records percent inhibition, a visual measurement of the effectiveness of each treatment by comparison with untreated plants. Inhibition of 0% indicates no effect, and inhibition of 100% indicates that all of the plants are completely dead. Inhibition of 85% or more is in most cases considered acceptable for normal herbicidal use; however in greenhouse tests such as the one described in this Example it is  
 20 normal to apply compositions at rates which are expected to give less than 85% inhibition, as this makes it easier to discriminate among compositions having different levels of effectiveness.

Results of the test of Example 20 are given in Table 7 below.

Table 7: Herbicidal effectiveness data for Example 20

Glyphosate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
MON 0139	200	8	70
	400	50	75
	600	78	85
	800	83	90
	1000	95	96

Glyphosate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
Roundup® Ultra (first set)	200	60	83
	400	75	98
	600	88	100
	800	99	100
	1000	98	100
Roundup® Ultra (second set)	200	65	83
	400	78	99
	600	91	99
	800	99	100
	1000	99	100
Composition of Example 19	200	55	73
	400	75	88
	600	96	98
	800	98	99
	1000	100	99

In this test the colloidal suspension of mono(N,N-distearyl-N-methylammonium) glyphosate (Example 19) provided herbicidal effectiveness greatly superior to that provided by the mono(isopropylammonium) salt (MON 0139) at equal glyphosate a.e. rates. On ABUTH, effectiveness of the composition of Example 19 was similar to that obtained with Roundup® Ultra, although the composition of Example 19 contains no added surfactant.

#### Example 21

Substantially the same procedure as used in Example 20 is followed, except where noted below, in a greenhouse test by foliar application to two representative annual broadleaf species, wild radish (*Raphanus sativus*, RAPSN) and tall morningglory (*Ipomoea purpurea*, PHBPU), a representative perennial narrowleaf species, quackgrass (*Elymus repens*, AGRRE). Soil is prefertilized with a 6-7-8 organic NPK fertilizer at a rate of 3.9 kg/m<sup>3</sup>. Plants receive 16 hours of light per day. Temperatures are maintained at approximately 23°C during the day and approximately 18°C during the night. Relative humidity is maintained at approximately 70%. Only one set of 3 replicates is assigned to Roundup® Ultra in this test. An early evaluation of herbicidal effectiveness is conducted 9 DAT, as an indication of enhanced early symptom development, as well as a later evaluation conducted 17 DAT. The compositions included in this test are those of

Examples 12 (comprising mono(dioctylammonium) glyphosate) and 19 (comprising mono(N,N-distearyl-N-methylammonium) glyphosate formulated with isopropanol and n-butanol as described above). Results of the test Example 21 are given in Table 8 below.

Table 8: Herbicidal effectiveness data for Example 21

Glyphosate composition	Glyphosate rate g a.e./ha	% Inhibition				
		9 DAT		17 DAT		
		RAPSN	PHBPU	AGRRE	RAPSN	PHBPU
MON 0139	360	20	15	18	43	37
	540	30	17	28	63	37
	720	20	15	37	60	42
Roundup® Ultra	360	28	18	70	67	45
	540	67	38	83	80	72
	720	42	18	90	77	53
Composition of Example 12	360	60	20	62	82	42
	540	67	18	83	83	52
	720	82	40	88	88	70
Composition of Example 19	360	35	15	48	77	38
	540	65	28	60	80	52
	720	40	27	80	82	62

5        In this test the colloidal suspension of mono(N,N-distearyl-N-methylammonium) glyphosate (Example 19) again provided herbicidal effectiveness greatly superior to that provided by the mono(isopropylammonium) salt (MON 0139) at equal glyphosate a.e. rates. The colloidal suspension of mono(dioctylammonium) salt (Example 12) was even more effective. Early symptom development (9 DAT) was more pronounced on RAPSN  
 10      with the composition of Example 12 than with Roundup® Ultra. By 17 DAT, herbicidal effectiveness of both colloidal suspension compositions was at least comparable to that of Roundup® Ultra, except for the composition of Example 19 on AGRRE.

#### Example 22

Substantially the same procedure as used in Example 20 is followed in a  
 15      greenhouse test by foliar application to ABUTH and ECHCF. Evaluation of herbicidal effectiveness is conducted 15 DAT. The compositions included in this test are those of Examples 13 (comprising mono(trihexylammonium) glyphosate), 14 (comprising mono(N,N-dioctyl-N-methylammonium)      glyphosate),      16      (comprising mono(dilaurylammonium)      glyphosate),      17      (comprising mono(N,N-dilauryl-N-

methylammonium) glyphosate and 18 (comprising mono(N,N-distearyl-N-methylammonium) glyphosate). Results of the test of Example 22 are given in Table 9 below.

Table 9: Herbicidal effectiveness data for Example 22

Glyphosate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
MON 0139	200	0	50
	400	2	62
	600	43	75
	800	72	77
	1000	83	85
Roundup® Ultra (first set)	200	5	67
	400	33	73
	600	75	82
	800	87	85
	1000	90	96
Roundup® Ultra (second set)	200	20	50
	400	57	60
	600	72	83
	800	88	93
	1000	95	94
Composition of Example 13	200	17	32
	400	40	40
	600	60	47
	800	78	57
	1000	78	63
Composition of Example 14	200	18	30
	400	13	27
	600	43	32
	800	57	42
	1000	77	40
Composition of Example 16	200	47	50
	400	78	60
	600	83	70
	800	92	72
	1000	92	73
Composition of Example 17	200	20	30
	400	10	43
	600	63	50
	800	75	60
	1000	82	62

Glyphosate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
Composition of Example 18	200	2	50
	400	50	53
	600	87	72
	800	96	75
	1000	95	80

In this test the colloidal suspensions of mono(dilauryl ammonium) glyphosate (Example 16) and mono(N,N-distearyl-N-methylammonium) glyphosate (Example 18) provided herbicidal effectiveness on ABUTH that was superior not only to that provided by the mono(isopropylammonium) salt (MON 0139), but also to that provided by 5 Roundup® Ultra, at equal glyphosate a.e. rates. The performance of the composition of Example 16 was especially noteworthy in this regard. However, none of the colloidal suspension formulations exhibited herbicidal effectiveness on ECHCF matching that of Roundup® Ultra. Herbicidal effectiveness of the colloidal suspension of mono(N,N-diethyl-N-methylammonium) glyphosate (Example 14) was notably weak on both test 10 species in this test.

#### Example 23

Substantially the same procedure as used in Example 21 is followed in a greenhouse test by foliar application to RAPSN, PHBPU and AGRRE. Only one set of 3 replicates is assigned to Roundup® Ultra in this test. An early evaluation of herbicidal 15 effectiveness is conducted 5 DAT, as an indication of enhanced early symptom development, as well as a later evaluation conducted 22 DAT. The compositions included in this test are those of Examples 13 (comprising mono(trihexylammonium) glyphosate), 14 (comprising mono(N,N-diethyl-N-methylammonium) glyphosate), 16 (comprising mono(dilauryl ammonium) glyphosate), 17 (comprising mono(N,N-dilauryl-N-methylammonium) 20 glyphosate and 18 (comprising mono(N,N-distearyl-N-methylammonium) glyphosate). Results of the test of Example 23 are given in Table 10 below.

Table 10: Herbicidal effectiveness data for Example 23

Glyphosate composition	Glyphosate rate g.a.e./ha	% Inhibition				
		5 DAT		22 DAT		
		RAPSN	PHBPU	AGRRE	RAPSN	PHBPU
MON 0139	360	10	18	43	28	30
	540	10	15	55	35	32
	720	10	17	47	40	32
Roundup® Ultra	360	17	20	67	47	73
	540	30	23	67	63	80
	720	23	38	75	88	95
Composition of Example 13	360	45	50	42	53	50
	540	63	55	62	60	68
	720	60	60	70	67	78
Composition of Example 14	360	30	52	53	67	80
	540	47	55	60	55	88
	720	62	52	77	89	85
Composition of Example 16	360	15	15	62	55	62
	540	20	32	73	92	90
	720	32	30	80	83	87
Composition of Example 17	360	15	28	65	85	58
	540	15	35	70	88	82
	720	15	60	70	92	90
Composition of Example 18	360	25	15	70	77	48
	540	15	15	78	85	47
	720	33	15	90	92	57

In this test four colloidal suspension compositions, those of Examples 14, 16, 17 and 18, outperformed Roundup® Ultra on RAPSN, as evaluated 22 DAT. The colloidal suspension of mono(N,N-distearyl-N-methylammonium) glyphosate (Example 18) also 5 outperformed Roundup® Ultra on RAPSN but was notably weak on PHBPU. The colloidal suspension of mono(trihexylammonium) glyphosate (Example 13) performed poorly on all three species in this test, although early symptom development as evaluated 5 DAT was much greater than that with Roundup® Ultra. The colloidal suspension of mono(N,N-dioctyl-N-methylammonium) glyphosate (Example 14) also gave pronounced 10 early symptom development. It is possible that early symptom development reflects acute injury to leaves by the cationic entity that inhibits longer-term effectiveness of glyphosate, for example by reduced translocation of the glyphosate from injured leaves.

Example 24

Substantially the same procedure as used in Example 20 is followed in a greenhouse test by foliar application to ABUTH and ECHCF. Evaluation of herbicidal effectiveness is conducted 21 DAT. The compositions included in this test are those of Examples 16 (comprising mono(dilaurylammmonium) glyphosate) and 18 (comprising mono(N,N-distearyl-N-methylammonium) glyphosate). Results of the test of Example 24 are given in Table 11 below.

Table 11: Herbicidal effectiveness data for Example 24

Glyphosate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
MON 0139	200	0	50
	400	20	77
	600	45	87
	800	47	88
	1000	73	95
Roundup® Ultra (second set)	200	10	80
	400	40	97
	600	60	99
	800	90	100
	1000	98	100
Roundup® Ultra (first set)	200	25	77
	400	50	95
	600	63	98
	800	92	100
	1000	100	100
Composition of Example 16	200	10	60
	400	40	82
	600	57	96
	800	67	97
	1000	73	94
Composition of Example 18	200	3	70
	400	37	83
	600	85	93
	800	88	100
	1000	100	100

In this test the high degree of herbicidal effectiveness of the colloidal suspension of mono(N,N-distearyl-N-methylammonium) glyphosate (Example 18) on ABUTH seen in the test of Example 22 was confirmed. Effectiveness equal to that of Roundup® Ultra was

exhibited by this formulation on ECHCF. However, in this test, performance of the colloidal suspension of mono(dilauryl ammonium) glyphosate (Example 16) was relatively weak.

Example 25

Substantially the same procedure as used in Example 20 is followed in a greenhouse test by foliar application to ABUTH and ECHCF. Evaluation of herbicidal effectiveness is conducted 16 DAT. The composition of Example 15 (comprising mono(didecyl ammonium) glyphosate) is included in this test. Results of the test of Example 25 are given in Table 12 below.

10

Table 12: Herbicidal effectiveness data for Example 25

Glyphosate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
MON 0139	200	5	27
	400	53	52
	600	70	67
	800	78	78
	1000	95	78
Roundup® Ultra (first set)	200	30	62
	400	60	73
	600	83	83
	800	93	97
	1000	98	97
Roundup® Ultra (second set)	200	33	57
	400	67	67
	600	83	77
	800	87	85
	1000	95	92
Composition of Example 15	200	28	10
	400	42	53
	600	80	60
	800	83	63
	1000	90	65

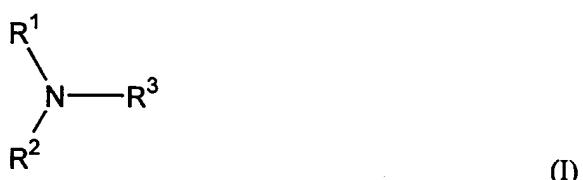
In this test the colloidal suspension of mono(didecyl ammonium) glyphosate (Example 15) provided superior herbicidal effectiveness to mono(isopropyl ammonium) glyphosate (MON 0139) on ABUTH, but was weaker in this regard than Roundup® Ultra.

On ECHCF the performance of the composition of Example 15 did not even match that of MON 0139.

The preceding description of specific embodiments of the present invention is not intended to be a complete list of every possible embodiment of the invention. Persons skilled in this field will recognize that modifications can be made to the specific embodiments described here that remain within the scope of the present invention.

## WHAT IS CLAIMED IS:

1. A plant treatment composition for application to foliage of a plant to elicit a desired biological response, comprising an aqueous application medium wherein are colloidally dispersed supramolecular aggregates comprising one or more amphiphilic salt(s) having anions of an anionic exogenous chemical substance and cations derived by protonation of one or more amine compound(s) each having the formula 5 (I)



10 wherein  $\text{R}^1$  and  $\text{R}^2$  are independently linear hydrocarbyl chains each having 6 to about 22 carbon atoms, and  $\text{R}^3$  is hydrogen, a  $\text{C}_{1-5}$  hydrocarbyl group or a linear hydrocarbyl chain no longer than  $\text{R}^1$  and no longer than  $\text{R}^2$ ; said composition containing the exogenous chemical substance in a first molar amount  $X^1$  in the form of said amphiphilic salt(s) and in a zero or second molar amount  $X^2$  in the form of one or more salt(s) having anions of the exogenous chemical substance and cations 15 derived from one or more base(s) other than an amine compound of formula (I); the total molar amount ( $X^1 + X^2$ ) of the exogenous chemical substance in salt form being sufficient to elicit said desired biological response when the composition is applied to the foliage of the plant at a rate from about 10 to about 1000 liters per hectare (l/ha), and  $X^1$  as a fraction of ( $X^1 + X^2$ ) being about 0.01 to 1.

20 2. The composition of Claim 1 wherein the exogenous chemical substance is a herbicide, plant growth regulator or nematicide that is systemic in plants.

3. The composition of Claim 1 wherein the exogenous chemical substance is a nematicide selected from 3,4,4-trifluoro-3-butenoic acid and N-(3,4,4-trifluoro-1-oxo-3-butenyl)glycine.

25 4. The composition of Claim 1 wherein the exogenous chemical substance is a herbicide.

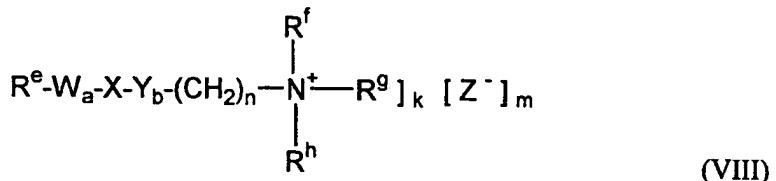
5. The composition of Claim 4 wherein the herbicide is selected from acifluorfen, asulam, benazolin, bentazon, bilanafos, bromacil, bromoxynil, chloramben, clopyralid, 2,4-D, 2,4-DB, dalapon, dicamba, dichlorprop, diclofop, endothall, fenac, fenoxyprop, flamprop, fluazifop, flumiclorac, fluoroglycofen, fomesafen, fosamine, glufosinate, glyphosate, haloxyfop, imazameth, imazamethabenz, imazapyr, imazaquin, imazethapyr, ioxynil, MCPA, MCPB, mecoprop, methylarsonic acid, naptalam, nonanoic acid, picloram, quinclorac, quizalofop, sulfamic acid, 2,3,6-TBA, TCA and triclopyr.
6. The composition of Claim 4 wherein the herbicide is an imidazolinone herbicide.
- 10 7. The composition of Claim 4 wherein the herbicide is selected from N-phosphonomethylglycine and DL-homoalanin-4-yl(methyl)phosphinate.
8. The composition of Claim 1 wherein said amine compound has a molecular weight of about 240 to about 700.
9. The composition of Claim 1 wherein said amine compound has a molecular weight 15 greater than about 300 and not greater than about 560.
10. The composition of Claim 1 wherein, in the formula for said amine compound, R<sup>1</sup> and R<sup>2</sup> are saturated or unsaturated hydrocarbyl chains each having independently 12, 14, 16 or 18 carbon atoms and R<sup>3</sup> is hydrogen or a methyl group.
11. The composition of Claim 10 wherein R<sup>1</sup> and R<sup>2</sup> chains are alike, and are derived 20 from natural fatty acids.
12. The composition of Claim 1 wherein said amine compound is N,N-dilauryl-N-methylamine.
13. The composition of Claim 1 wherein said amine compound is N,N-distearyl-N-methylamine.
- 25 14. The composition of Claim 1 wherein X<sup>2</sup> is zero.
15. The composition of Claim 1 wherein X<sup>2</sup> > 0 and the cations derived from said base(s) other than an amine compound of formula (I) are monovalent cations selected from (i) alkali metal cations, (ii) ammonium cations, (iii) alkylammonium, alkanolammonium and alkanolalkylammonium cations having 1-5 carbon atoms, (iv)

alkylsulfonium cations having 1-5 carbon atoms, and (v) cations derived from an amine compound of formula (II):



wherein R<sup>4</sup> and R<sup>5</sup> are independently hydrogen, methyl groups or hydrocarbyl chains each having 2 to 5 carbon atoms, and R<sup>6</sup> is a linear hydrocarbyl chain having 6 to about 22 carbon atoms.

- 5 16. The composition of Claim 15 wherein said monovalent cations are selected from sodium, ammonium, dimethylammonium, isopropylammonium, monoethanolammonium, trimethylsulfonium, octylammonium, N-lauryl-N,N-dimethylammonium and N-stearyl-N,N-dimethylammonium cations.
- 10 17. The composition of Claim 1 wherein X<sup>1</sup> as a fraction of (X<sup>1</sup> + X<sup>2</sup>) is about 0.01 to about 0.2.
- 18. The composition of Claim 1 wherein X<sup>1</sup> as a fraction of (X<sup>1</sup> + X<sup>2</sup>) is about 0.1 to 1.
- 19. The composition of Claim 1 wherein X<sup>1</sup> as a fraction of (X<sup>1</sup> + X<sup>2</sup>) is about 0.3 to 1.
- 15 20. The composition of Claim 1, further comprising an adjuvant amount of an amphiphilic quaternary ammonium compound, or mixture of such compounds, each having formula (VIII):



wherein R<sup>e</sup> is a hydrocarbyl or haloalkyl group having about 6 to about 22 carbon atoms; W and Y are independently O or NH; a and b are independently 0 or 1 but at least one of a and b is 1; X is CO, SO or SO<sub>2</sub>; n is 2 to 4; R<sup>f</sup>, R<sup>g</sup> and R<sup>h</sup> are independently C<sub>1-4</sub> alkyl; Z<sup>-</sup> is a suitable anion; and k and m are integers such that the positive electrical charges on cations balance the negative electrical charges on anions.

21. The composition of Claim 20 wherein, in the formula for said amphiphilic quaternary ammonium compound or mixture of such compounds, R<sup>c</sup> is a saturated perfluoroalkyl group having about 6 to about 12 carbon atoms, X is SO<sub>2</sub>, Y is NH, a is 0, b is 1, n is 3, R<sup>f</sup>, R<sup>g</sup> and R<sup>h</sup> are methyl groups, k and m are each 1, and Z<sup>-</sup> is a chloride, bromide or iodide anion.

5

22. The composition of Claim 1, further comprising an adjuvant amount of an oil or mixture of oils.

23. The composition of Claim 22 wherein said oil(s) each have a chemical structure corresponding to formula (IX):

10



wherein R<sup>14</sup> is a hydrocarbyl group having about 5 to about 21 carbon atoms, R<sup>15</sup> is a hydrocarbyl group having 1 to about 14 carbon atoms, the total number of carbon atoms in R<sup>14</sup> and R<sup>15</sup> is about 11 to about 27, and Y is O or NH.

15

24. The composition of Claim 23 wherein said oil(s) are selected from methyl oleate, ethyl oleate, isopropyl myristate, isopropyl palmitate and butyl stearate.

25. A liquid concentrate composition that comprises about 5% to about 40% by weight of an anionic exogenous chemical substance expressed as acid equivalent, and that when diluted with a suitable amount of water forms a plant treatment composition of Claim 1.

20 26. An aqueous concentrate composition that comprises about 5% to about 40% by weight of an anionic exogenous chemical substance expressed as acid equivalent, and that when diluted with a suitable amount of water forms a plant treatment composition of Claim 1.

27. A herbicidal composition for application to foliage of a plant, comprising an aqueous application medium wherein are colloidally dispersed supramolecular aggregates comprising one or more amphiphilic salt(s) having anions of N-phosphomethylglycine and cations derived by protonation of one or more amine compound(s) each having the formula (I)

25



wherein R<sup>1</sup> and R<sup>2</sup> are independently linear hydrocarbyl chains each having 6 to about 22 carbon atoms, and R<sup>3</sup> is hydrogen, a C<sub>1-5</sub> hydrocarbyl group or a linear hydrocarbyl chain no longer than R<sup>1</sup> and no longer than R<sup>2</sup>; said composition containing said N-phosphonomethylglycine in a first molar amount X<sup>1</sup> in the form of said amphiphilic salt(s) and in a zero or second molar amount X<sup>2</sup> in the form of one or more salt(s) having anions of N-phosphonomethylglycine and cations derived from one or more base(s) other than an amine compound of formula (I); the total molar amount (X<sup>1</sup> + X<sup>2</sup>) of N-phosphonomethylglycine in salt form being sufficient to elicit a herbicidal response when the composition is applied to the foliage of the plant at a rate from about 10 to about 1000 liters per hectare (l/ha), and X<sup>1</sup> as a fraction of (X<sup>1</sup> + X<sup>2</sup>) being about 0.01 to 1.

10            28. The composition of Claim 27 wherein said amine compound has a molecular weight of about 240 to about 700.

15            29. The composition of Claim 27 wherein said amine compound has a molecular weight greater than about 300 and not greater than about 560.

20            30. The composition of Claim 27 wherein, in the formula for said amine compound, R<sup>1</sup> and R<sup>2</sup> are saturated or unsaturated hydrocarbyl chains each having independently 12, 14, 16 or 18 carbon atoms and R<sup>3</sup> is hydrogen or a methyl group.

25            31. The composition of Claim 30 wherein R<sup>1</sup> and R<sup>2</sup> chains are alike, and are derived from natural fatty acids.

32. The composition of Claim 27 wherein said amine compound is N,N-dilauryl-N-methylamine.

33. The composition of Claim 27 wherein said amine compound is N,N-distearyl-N-methylamine.

34. The composition of Claim 27 wherein X<sup>2</sup> is zero.

35. The composition of Claim 27 wherein  $X^2 > 0$  and the cations derived from said base(s) other than an amine compound of formula (I) are monovalent cations selected from (i) alkali metal cations, (ii) ammonium cations, (iii) alkylammonium, alkanolammonium and alkanolalkylammonium cations having 1-5 carbon atoms, (iv) alkylsulfonium cations having 1-5 carbon atoms, and (v) cations derived from an amine compound of formula (II):



wherein  $R^4$  and  $R^5$  are independently hydrogen, methyl groups or hydrocarbyl chains each having 2 to 5 carbon atoms, and  $R^6$  is a linear hydrocarbyl chain having 6 to about 22 carbon atoms.

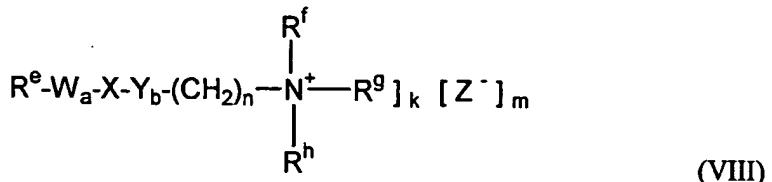
10 36. The composition of Claim 35 wherein said monovalent cations are selected from sodium, ammonium, dimethylammonium, isopropylammonium, monoethanolammonium, trimethylsulfonium, octylammonium, N-lauryl-N,N-dimethylammonium and N-stearyl-N,N-dimethylammonium cations.

15 37. The composition of Claim 27 wherein  $X^1$  as a fraction of  $(X^1 + X^2)$  is about 0.01 to about 0.2.

38. The composition of Claim 27 wherein  $X^1$  as a fraction of  $(X^1 + X^2)$  is about 0.1 to 1.

39. The composition of Claim 27 wherein  $X^1$  as a fraction of  $(X^1 + X^2)$  is about 0.3 to 1.

20 40. The composition of Claim 27, further comprising an adjuvant amount of an amphiphilic quaternary ammonium compound, or mixture of such compounds, each having formula (VIII):



wherein  $R^e$  is a hydrocarbyl or haloalkyl group having about 6 to about 22 carbon atoms; W and Y are independently O or NH; a and b are independently 0 or 1 but at

least one of a and b is 1; X is CO, SO or SO<sub>2</sub>; n is 2 to 4; R<sup>f</sup>, R<sup>g</sup> and R<sup>h</sup> are independently C<sub>1-4</sub> alkyl; Z<sup>-</sup> is a suitable anion; and k and m are integers such that the positive electrical charges on cations balance the negative electrical charges on anions.

- 5      41. The composition of Claim 40 wherein, in the formula for said amphiphilic quaternary ammonium compound or mixture of such compounds, R<sup>e</sup> is a saturated perfluoroalkyl group having about 6 to about 12 carbon atoms, X is SO<sub>2</sub>, Y is NH, a is 0, b is 1, n is 3, R<sup>f</sup>, R<sup>g</sup> and R<sup>h</sup> are methyl groups, k and m are each 1, and Z<sup>-</sup> is a chloride, bromide or iodide anion.
- 10     42. The composition of Claim 27, further comprising an adjuvant amount of an oil or mixture of oils.
- 43. The composition of Claim 42 wherein said oil(s) each have a chemical structure corresponding to formula (IX):



- 15     wherein R<sup>14</sup> is a hydrocarbyl group having about 5 to about 21 carbon atoms, R<sup>15</sup> is a hydrocarbyl group having 1 to about 14 carbon atoms, the total number of carbon atoms in R<sup>14</sup> and R<sup>15</sup> is about 11 to about 27, and Y is O or NH.
- 44. The composition of Claim 43 wherein said oil(s) are selected from methyl oleate, ethyl oleate, isopropyl myristate, isopropyl palmitate and butyl stearate.
- 20     45. An aqueous concentrate composition that comprises about 5% to about 40% by weight of an anionic exogenous chemical substance expressed as acid equivalent, and that when diluted with a suitable amount of water forms a herbicidal composition of Claim 27.
- 25     46. A process for making a liquid concentrate composition of an exogenous chemical substance, comprising a neutralizing step and a conditioning step; wherein the neutralizing step comprises neutralization of a first molar amount X<sup>1</sup> of an anionic exogenous chemical substance with one or more amine compound(s) in a liquid medium with agitation to make a liquid composition containing one or more amphiphilic salt(s) of the exogenous chemical substance; and wherein the conditioning step comprises continuing the agitation of the liquid composition until

supramolecular aggregates comprising said amphiphilic salt(s) of the exogenous chemical substance are colloidally dispersed in the liquid medium to form a stable suspension; said amine compound(s) having a chemical structure corresponding to formula (I)



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wherein  $R^1$  and  $R^2$  are independently linear hydrocarbyl chains each having 6 to about 22 carbon atoms, and  $R^3$  is hydrogen, a  $C_{1-5}$  hydrocarbyl group or a linear hydrocarbyl chain no longer than  $R^1$  and no longer than  $R^2$ .

- 47. The process of Claim 46 wherein said neutralizing step further comprises introducing to the liquid composition, with agitation, a second molar amount  $X^2$  of the exogenous chemical substance in the form of one or more salt(s) other than an amphiphilic salt formed by neutralizing the exogenous chemical substance with an amine compound of formula (I); and wherein  $X^1$  as a fraction of  $(X^1 + X^2)$  is about 0.01 to 1.
- 10 48. The process of Claim 47 wherein the salt(s) of the second molar amount of the exogenous chemical substance are made *in situ* by neutralizing, in the liquid medium with agitation, said second molar amount with one or more base(s) other than an amine compound of formula (I), before, during or after neutralization of the first molar amount.
- 15 49. The process of any of Claims 46 to 48 wherein the liquid medium is an aqueous medium.
- 20 50. A process for making an aqueous concentrate composition of N-phosphonomethylglycine comprising a neutralizing step and a conditioning step; wherein the neutralizing step comprises adding to water a first molar amount  $X^1$  of N-phosphonomethylglycine in acid form, together with an amine compound in an amount of about 1 to about 2 moles per mole of N-phosphonomethylglycine, to make an amphiphilic salt comprising a monobasic salt, a dibasic salt, or a mixture of such monobasic and dibasic salts; and wherein the conditioning step comprises continuing
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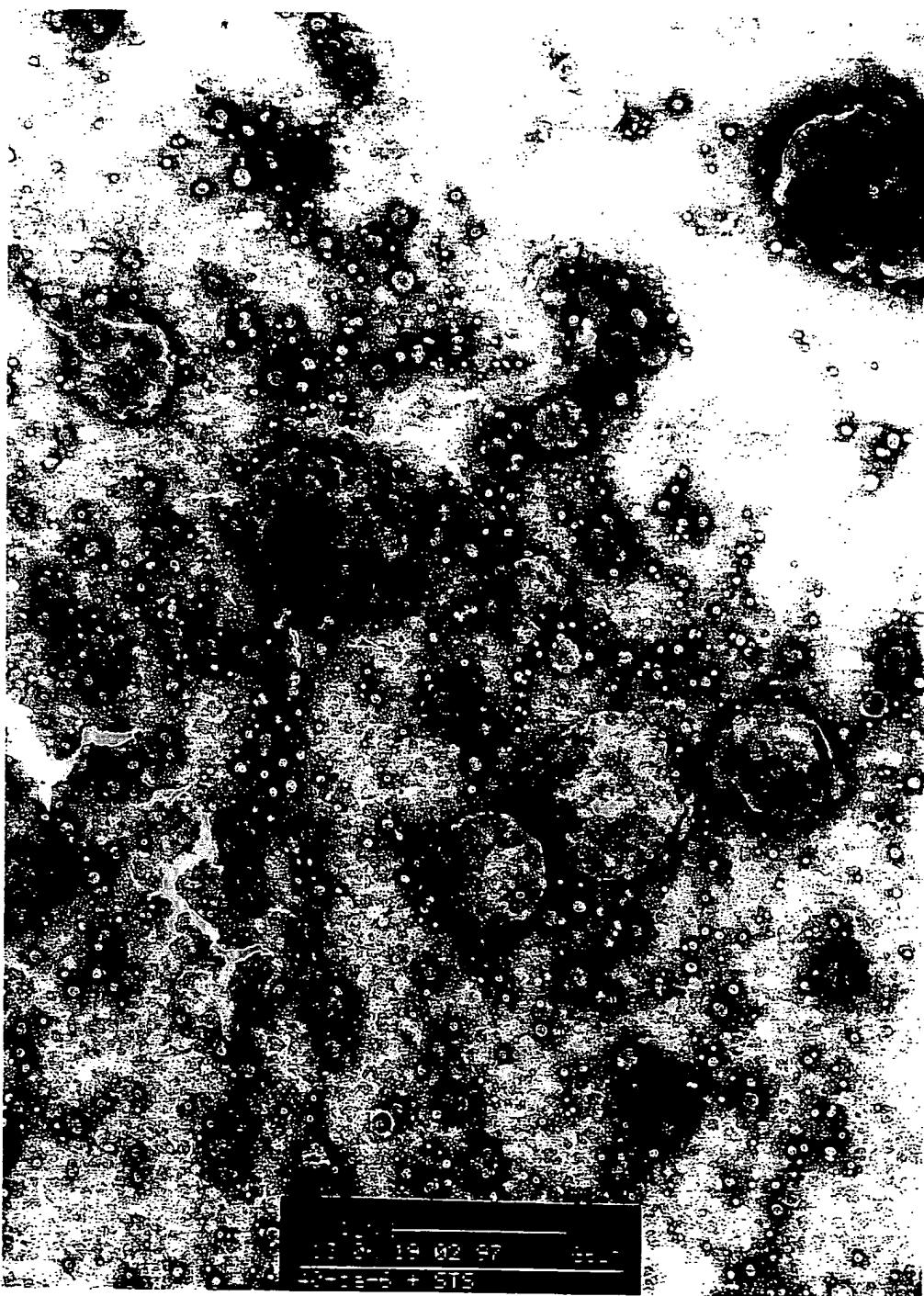
the agitation of the liquid composition until supramolecular aggregates comprising said amphiphilic salt of N-phosphonomethylglycine are colloidally dispersed in the liquid medium to form a stable suspension; said amine compound(s) having a chemical structure corresponding to formula (I)



wherein R<sup>1</sup> and R<sup>2</sup> are independently linear hydrocarbyl chains each having 6 to about 22 carbon atoms, and R<sup>3</sup> is hydrogen, a C<sub>1-5</sub> hydrocarbyl group or a linear hydrocarbyl chain no longer than R<sup>1</sup> and no longer than R<sup>2</sup>.

- 5        51. The process of Claim 50 wherein said neutralizing step further comprises introducing to the liquid composition, with agitation, a second molar amount X<sup>2</sup> of N-phosphonomethylglycine in the form of a monobasic salt, a dibasic salt or a mixture of monobasic and dibasic salts, other than an amphiphilic salt formed by neutralizing N-phosphonomethylglycine with an amine compound of formula (I); and wherein X<sup>1</sup> as a fraction of (X<sup>1</sup> + X<sup>2</sup>) is about 0.01 to 1.
- 10      52. The process of Claim 51 wherein the salt of the second molar amount of N-phosphonomethylglycine is made *in situ* by neutralizing, in the liquid medium with agitation, said second molar amount with one or more base(s) other than an amine compound of formula (I), before, during or after neutralization of the first molar amount.
- 15      53. A process for eliciting a desired biological activity in a plant or in a pathogen, parasite or feeding organism present in or on a plant, comprising a step of applying to foliage of the plant a biologically effective amount of a plant treatment composition of any of Claims 1 to 24.
- 20      54. A process for killing or controlling undesired plants comprising a step of applying to foliage of the plants a herbicidally effective amount of a herbicidal composition of any of Claims 27 to 44.
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**SUBSTITUTE SHEET (RULE 26)**

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 98/11019

A. CLASSIFICATION OF SUBJECT MATTER		
IPC 6	A01N25/04	A01N25/30
		A01N57/20

According to International Patent Classification(IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 799 758 A (JOHN FRANZ) 26 March 1974 cited in the application see column 3, line 38 - column 4, line 14 -----	1-54
A	EP 0 124 351 A (STAUFFER CHEMICAL COMP) 7 November 1984 see claims -----	1-54
A	GB 2 098 481 A (ICI PLC) 24 November 1982 see page 1, line 22 - line 46 -----	1-54
A	FR 2 489 332 A (BORSODI VEGYI KOMB) 5 March 1982 see claims -----	1-26

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

28 September 1998

Date of mailing of the international search report

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